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Electro-based technologies for contaminants removal from soil and effluent targeting further reuses

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PREFACE

This dissertation is submitted as partial fulfilment of the requirements for the Doctoral Degree in Environment and Sustainability, and it includes the results of my Ph.D. study carried out from April 2015 to September 2018 in the Faculty of Sciences and Technology, Universidade NOVA de Lisboa, with the stay abroad as visiting researcher in the Department of Civil Engineering, Technical University of Denmark (DTU), Lyngby, Denmark (January-July 2016; August-December 2017; August-October 2018). I was also part of the KIC EIT Raw Materials labelled IDS-FunMat-INNO Doctoral Programme.

The dissertation is organized as follows:

Part I includes:

Section I - provides all the summarized information regarding the problem statement, main motivations and objectives of the work.

Section II - includes the description of material as methods used during this Ph.D.

Section III - compiles the major findings of the experimental work and examines some limitations.

Section IV - outlines the main conclusions and identifies future areas of research.

Appendices

Part II includes all the papers published, submitted or under preparation in the scope of this Ph.D. study, including material subject to IP protection.

Peer Reviewed papers (ISI/SCI):

1. Ferreira AR, Guedes P, Mateus EP, Ribeiro AB, Couto N (2017) Comparative assessment of LECA and Spartina maritima to remove emerging organic contaminants from wastewater. Environmental Science and Pollution Research, 24(8): 7208–7215, http://dx.doi.org/10.1007/s11356-017-8452-4

2. Ferreira AR, Guedes P, Mateus EP, Ribeiro AB, Couto N (2018) Electrodialytic 2-compartment cells for EOCs removal from effluent. Journal of Hazardous Materials, 358: 467-474, https://doi.org/10.1016/j.jhazmat.2018.04.066

3. Ferreira AR, Guedes P, Mateus EP, Ribeiro AB, Couto N (2017) Influence of the cell design in the electroremoval of PPCPs from soil slurry. Chemical Engineering Journal, 326: 162-168, http://dx.doi.org/10.1016/j.cej.2017.05.148

Conference proceedgins:

4. Ferreira AR, Ottosen L, Couto N, Ribeiro A (2016) Remediation of As-contaminated soil - Comparison of two different electrodialytic cells and applicability in brick materials, Proceedings of the Materials, Systems and Structures in Civil Engineering (MSSCE 2016), Copenhagen, Denmark, August 2016, ISBN: 978-2-35158-176-6

Papers submitted or under preparation:

5. Ferreira AR, Couto N, Ribeiro AB, Ottosen L (*submitted*) Electrodialytic arsenic removal from bulk and pretreated soil.

6. Ferreira AR, Guedes P, Mateus EP, Ribeiro AB, Couto N (*under preparation*) Emerging organic contaminants in soil irrigated with effluent: electrokinetics as a remediation strategy

7. Ferreira AR, Guedes P, Mateus EP, Jensen PE, Ribeiro AB, Couto N (*under preparation*) Electrokinetic remediation of oil-contaminated soils in cold climate conditions.

IP protection material (potential):

1. Ferreira AR, Guedes P, Mateus EP, Ribeiro AB, Couto N (*under preparation*) Electrochemical degradation of emerging organic contaminants from effluent: electro-catalytic materials and design influence.

I hereby declare that, as the first author of the manuscripts mentioned above, I provided the major contribution to the research and experimental work developed, to the results interpretation and the preparation of these publications submitted during the Ph.D. project. The copyright of the publications was transferred to the editors, and these articles are reproduced with permission of the original publishers and subject to copy restrictions imposed by them. Also, legal issues that applies to under review/preparations papers and material under IP protection.

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ABSTRACT

Soil and water resources are interconnected, and their protection is essential to Human life. Emerging organic contaminants (EOC) are a large group of unregulated compounds, which presence in both soils and effluents is a matter of major concern with unknown consequences. Thus, in order to reduce environmental and human associated risks, there is a need to develop viable techniques for the removal of these contaminants.

In this Ph.D. dissertation, cost-effective key solutions based on electro-technologies were designed and studied for soil and effluent remediation, which are the downstream and upstream sources of the contamination. Soil remediation was focused on EOC and contamination legacy that is more resistant to natural attenuation (arsenic and petroleum hydrocarbons). The effluent treatment was focused on EOC removals and also the possibility to promote phosphorus recovery/reuse, a critical raw material essential to life.

The electrokinetic contaminants removal from soil was developed aiming its valorization either in agriculture or as a secondary raw material. Soil treatment was highly dependent on both soil and contaminants properties. More aggressive electro-treatment conditions were designed *ex-situ* using 1- to 3-compartment electrodialytic reactors with soil stirring. For all the cases, the electric current enhanced contaminants removal. Up to 80% of arsenic was removed from soil in a 2-compartment cell, whereas remediation experiments of EOC achieved at least a 44% removal (mobilized and/or degraded) for three tested set-ups. An *in-situ* treatment with different electrical current strategies aiming at less soil disturbance was also developed for more sensitive scenarios like agricultural soil and arctic environment. The removal of hydrocarbons in artic soil was challenged by a more recalcitrant contamination, whereas EOC remediation in agricultural soil was enhanced up to a 37% by the electric current.

The electro-technologies developed for effluent treatment were designed to promote a safer irrigation and/or environmental discharge. For either the reuse or the removal of phosphorus, together with EOC removal, a reactor with an anion exchange membrane with polarization switch showed to be the best approach developed (up to 15% P recovery and 57-72% of EOC removal). A one-compartment reactor with a sequence of more than two circular-shaped metal mixed oxide coated titanium mesh electrodes, alternated in polarity, was the best approach for EOC removal (up to 90% in 2 hours). This treatment does not require the addition of reagents and represents low energetic costs, making it more environmentally friendly.

The technologies based on electrokinetic treatment showed to have a high potential for a wide array of applications, although the selection of the suitable treatment setup should be done case-by-case.

Keywords: electro-based technologies, cell design, emerging organic contaminants, effluent, soil, legacy contamination

RESUMO

O solo e os recursos hídricos estão interligados e sua proteção é essencial para a vida Humana. Contaminantes emergentes (CE) são um vasto grupo de compostos não regulamentados, cuja presença em solo e efluente é uma questão de grande preocupação com consequências desconhecidas. Assim, com o objetivo de reduzir os riscos associados tanto a nivel ambiental como de saúde pública, é necessário desenvolver técnicas viáveis para a remoção destes contaminantes.

Nesta dissertação, soluções-chave de baixo custo com base em eletro-tecnologias foram projetadas e estudadas para remediação de solos e efluente, que são as fontes a jusante e a montante da contaminação, respetivamente. A remediação do solo foi focada nos CE e no legado de contaminação que é mais resistente à atenuação natural (arsénio e hidrocarbonetos de petróleo). O tratamento de efluente foi focado na remoção de CE e também na possibilidade de promover a recuperação / reutilização de fósforo.

A estratégia de remediação do solo através do processo eletrocinético foi desenvolvida visando a sua valorização tanto na agricultura como como matéria-prima secundária. O tratamento do solo foi altamente dependente das propriedades do solo e dos contaminantes. As condições mais agressivas do tratamento foram projetadas *ex-situ* testando diferentes tipos de células com agitação no compartimento do solo. Para todos os casos, a corrente elétrica potencializou a remoção de contaminantes. Até 80% do arsénio foi removido do solo em uma célula de 2-compartimentos, enquanto os ensaios de remediação com CE alcançaram pelo menos 44% de remoção (mobilização e / ou degradação) para as três configurações testadas (1 a 3 compartimentos). A possibilidade de tratamento in-situcom diferentes estratégias de corrente elétrica, com o objetivo de causar menor perturbação ao solo, também foi estudada para cenários mais sensíveis, como solo agrícola e ambiente ártico. A remoção de hidrocarbonetos em solo polar apresentou uma contaminação mais recalcitrante, enquanto a remediação de CE em solo agrícola foi aumentada até 37% pela corrente elétrica.

As eletro-tecnologias desenvolvidas para o tratamento de efluente foram projetadas para promover uma irrigação mais segura e / ou uma descarga ambiental. Para a reutilização ou remoção do fósforo, juntamente com a remoção de CE, um reator com membrana de troca anionica com interruptor de polarização mostrou ser a melhor abordagem desenvolvida (até 15% de recuperação de P e 57-72% de remoção de CE). Um reator de um compartimento com uma sequência de mais de dois eletrodos de malha de titânio revestidos com óxido misto de metal circular, alternados em polaridade, mostrou ser o melhor *set-up* para a remoção de CE (até 90% em 2 horas). Este tratamento não requer a adição de reagentes e representa baixos custos energéticos, tornando-o mais ecológico.

As tecnologias baseadas no tratamento eletrocinético mostraram ter um alto potencial para uma ampla gama de aplicações, embora a seleção da configuração de tratamento adequada deva ser feita caso a caso.

Palavras-chave: processo electrocinético, design de célula, contaminants emergentes, efluente, solo, legado de contaminação

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ABBREVIATIONS

ACN	acetonitrile
1C	one compartment
2C	two compartments
3C	three compartments
AOPs	advanced oxidation process
AEM	anion exchange membrane
AEM	anion exchange membrane
ALVT	águas *de Lisboa e Vale do Tejo*
AOP	advanced oxidation process
As	arsenic
BOD5	biochemical oxygen demand
BOD_5	biochemical oxygen demand
BPA	bisphenol A
CAF	caffeine
CBMP	carbamazepine
CC	continuous current
CEM	cation exchange membrane
COD	chemical oxygen demand
CWs	constructed wetalnds
DAD	diode array detector
DC	direct current
DCF	diclofenac
DSA	dimensionally stable anode
DTU	Technical University of Denmark
E2	17β-estradiol
EC	electric conductivity

ED	electrodialytic
EDR	electrodialytic remediation
EE2	17α-ethinylestradiol
EK	electrokinetic
EKR	electrokinetic remediation
EOC	emerging organic contaminants
EOF	electroosmotic flux
EU	European Union
FAO	food and agriculture organization
FF	fine fraction
GC-MS	gas chromatography coupled to mass spectrometry
HPLC	high-performance liquid chromatography
IBF	ibuprofen
ICP-OES	inductively copled plasma - optical emission spectrometer
IEM	ion exchange membrane
k	constant of velocity
K_{ow}	octanol-water partition coefficient
LC	liquid chromatography
LD	limit of detection
LECA	light expanded clay aggregate
LQ	limit of quantification
MBPh	oxybenzone
MMO	mixed metal oxides
MPV	maximum permissible values
P	phosphorus
PAHs	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PHs	petroleum hydrocarbons

PPCPs	pharmaceuticals and personal care products
PTFE	polytetrafluoroethylene
QuEChERS	quick easy cheap effective rugged safe
REP	reversed electrode polarization
RMV	recommended maximum values
RSD	relative standard deviation
SCE	saturated calomel electrode
SD	standard deviation
SEM-EDX	scanning electron microscopy with energy dispersive X-ray spectroscopy
SFM	sulfamethoxazole
SPE	solid phase extraction
TPHs	total petroleum hydrocarbons
USDA	United States department of agriculture
WHO	world health organization
WWTP	wastewater treatment plant

PART I

SECTION I

1. INTRODUCTION

1.1. Legacy contamination in soil

1.1.1. Background

Soil is a non-renewable resource, meaning its loss and degradation is not recoverable within human lifespan. Soil is core component of land resources, agricultural development and ecological sustainability and for many critical ecosystem services. It is therefore a highly valuable natural resource, that needs to be recognized and valued for their productive capacities, as well as, their contribution to food security and the maintenance of key ecosystem services.

The current world population is around 7.7 billion, and the demographic trends projected a growth in global population to exceed 9 billion by 2050 (UN, 2015). Thus, it is estimated that by 2050, agricultural production must increase by 60% globally – and by almost 100% in developing countries – in order to meet food demand alone (FAO, 2015). Agriculture already uses 11% of the world's land surface for crop production. *The Status of the World's Soil Resources* produced by Food and Agriculture Organization (FAO) of the United Nations, Intergovernmental Technical Panel on Soils (FAO, 2015) reported that 33% of soil is moderately to highly degraded due to erosion, nutrient depletion, acidification, salinization, compaction and chemical pollution. This means that there is a threat of not corresponding to the basic needs in the future because the additional available land is not suitable for agriculture, and the ecological, social and economic costs of bringing it into production will be very high.

Sustainable management of the world's agricultural soils and sustainable production have therefore become imperative for reversing the trend of soil degradation and ensuring current and future global food security. A shortage of any nutrient required for plant growth can limit crop yield. It was estimated that a more efficient use of water, reduced use of pesticides and improvements in soil health can lead to average crop yield increases of 79% (FAO, 2015).

In the scope of the 7th Environment Action Programme – The new general Union Environment Action Programme to 2020, half a million of contaminated sites were identified in all European Union (EU), i.e. where the presence of dangerous substances has been confirmed. These sites may represent potential threats to human health, water bodies, soil, habitats, foodstuffs and biodiversity (APA, 2018).

The soil contamination is a result of anthropogenic activities, which the main causes of contamination are related to industrial production and commercial activities, as well as, industrial and municipal waste treatment and disposal (EEA, 2017). Figure 1.1 shows the overview of contaminants affecting soil in Europe. The most frequent soil contaminants detected are heavy metals and mineral oil corresponding to 37.3% and 33.7%, respectively at the investigated sites.

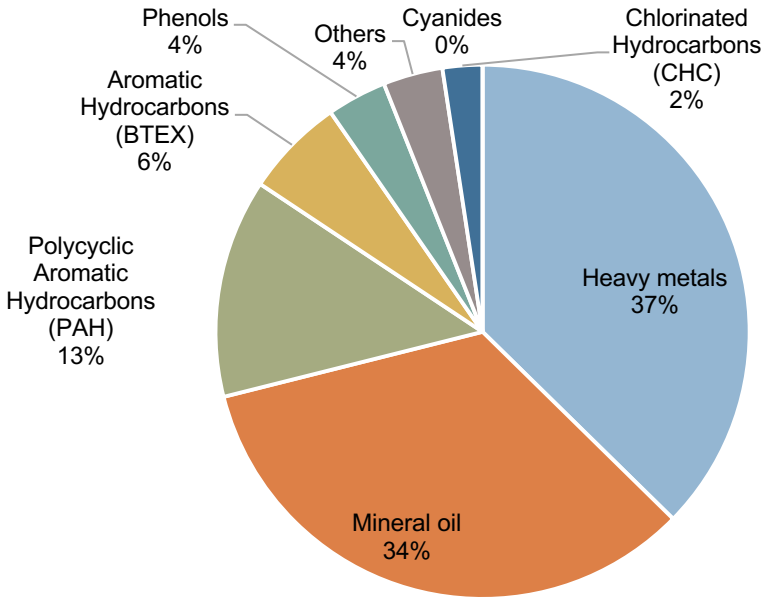


Figure 1.1 - Overview of contaminants affecting soil in Europe (*EEA, European Environment Agency*, 2017).

1.1.2. Arsenic

Arsenic (As) is on top 10 of the chemicals of major concern considered by World Health Organization (WHO, 2018). As is a metalloid naturally found in the environment, but its wide presence in soils in problematic concentrations is mainly due to anthropogenic activities. Mining activity, combustion of fossil fuels, industry activities, intensive agriculture practices by application of pesticides and fertilizers, and irrigation with wastewater resulting from industrial activities (e.g. mining) have provoked the dissemination of As in soils (Ungureanu et al., 2015).

Soil pollution by As is strongly linked to the wood preservation industry. The treated wood is impregnated with organic and/or inorganic preservative agents in order to protect the wood and to enhance its lifetime service. This preservative agent is made of copper oxide (CuO), chromium oxide (CrO_3) and arsenic oxide (As_2O_5). The leaching from wood when exposed to the rainfall or climatic conditions and/or particles dispersion from the treated wood contributing to As dispersion in soil. Arsenic is the element of the three that causes greatest concern due to the toxicity even at very low levels. Background levels depend on the local conditions and independent of this there is a geographical variation. On a global scale the natural background for arsenic is less than 10 mg kg^{-1} soil.

Once in soils, bioavailable concentrations of As can be widespread. This contaminant have been detected in groundwater and there are a number of regions where As contamination of drinking-water is significant (Argos et al., 2010). Besides the water, it has been reported that millions of people worldwide suffered from As toxicity due to the intake of As-contaminated food (Li et al., 2016). The long-term irrigation of land or the intensive agriculture due to pesticides and fertilizers application can result

in As accumulation in the soil and accumulation in vegetables and crop tissues being magnified with increased trophic level (Arco-Lázaro et al., 2016; Sharma et al., 2016; Wuana and Okieimen, 2011). For irrigation water, Portuguese legislation (Decree-Law 306/2007) relates recommended maximum values (RMV) and maximum permissible values (MPV) for As concentrations (MPV: 10 μg L^{-1}), also containing the observation that toxicity varies depending on the crop. The amount of As ingested daily by humans via food is greatly influenced by the amount of food in the diet, e.g.: high consumers of rice in Europe, such as certain ethnic groups, are estimated to have a daily dietary exposure of As about 1 μg kg^{-1} b.w. *per* day, and there is an increasing interest of rice as a potential source of As exposure due to its large daily consumption (Singh et al., 2015). The metalloid As is a toxic and carcinogenic element thus, the removal from agricultural soils and the prevention of its entrance is of unquestionable importance. The contamination of soils by As is a major problem encountered in many countries around the world and the management of these sites has been studied over the last years. The adverse health effects and the negative environmental impact explains the increased interest in As abundance, behavior and remediation over the years being considered a legacy contaminant of emerging interest (Sauvé and Desrosiers, 2014).

1.1.3. Petroleum hydrocarbons

The persistence of hydrophobic organic compounds, as petroleum hydrocarbons (PHs), in soils is a matter of significant public, scientific and regulatory concerns because of their potential toxicity, mutagenicity, carcinogenicity and ability to be bioaccumulated and biomagnified in the food chain (Sun et al., 2016).

PHs are complex mixtures of hundreds of hydrocarbon compounds that can be divided into four major groups: alkanes, aromatics, resins, and asphaltenes. In general, an alkane fraction is the most biodegradable, whereas the polar fraction (i.e., resins and asphaltenes) is more resistant to biological degradation. Most of them are persistent in the natural environment, due to their slow degradation by natural attenuation or (photo) chemical/biological processes. The physico-chemical properties of oil, such as hydrophobic nature with very low water solubility and high octanol-water partition coefficient, difficult the removal of these compounds as they adsorb tightly to soil organic matter making them less susceptible to biological and chemical degradation (Trellu et al., 2016).

The use of crude oil, all over the world serves as source of fuel and energy. Accidental spills, discharges or even leaks of PHs can result in large quantities of soil spread contamination, representing a significant environmental concern.

PHs been found occurring in air, soil, surface water, groundwater and sediments (Alegbeleye et al., 2017). The fate of the hydrocarbons in the environment and the routes of wildlife or human exposure are influenced by the environmental medium. However, some environments are more sensitive than others, such as, the Arctic environment that is very fragile to anthropogenic disturbances due to slow recovery times (Jorgenson et al., 2010). Human activities in Polar Regions (continental Antarctica and regions lying north of the tree line in the Arctic) are quite dependent of PHs for power generation,

heating and operation of vehicles, aircraft and ships. In addition, it has been reported that oil spills have become a serious problem in cold environments with the ever-increasing resource exploitation, transportation, storage, and accidental leakage of oil. Several techniques, including physical, chemical, and biological methods, were studied to remove spilled oil from the environment but the challenges and constraints in cold environments remain large (Yang et al., 2009).

1.2. Emerging organic organic contaminants in the environment

Emerging organic contaminants (EOC) or contaminants of emerging concern, can be defined as naturally occurring, manufactured or manmade chemicals or materials, which the lack of data about environmental fate and ecotoxicological or toxicological effects, prevent the proper evaluation of associated risks (Naidu et al., 2016; Sauvé and Desrosiers, 2014). EOC might pose risks but are not yet subjected to regulatory criteria or norms for the protection of human health or the environment. The contaminant remains “emerging” as long as there is a scarcity of information in the scientific literature or there are poorly documented issues about the associated potential problems they could cause (Naidu et al., 2016; Sauvé and Desrosiers, 2014).

EOC broadly comprise ‘lifestyle compounds’, personal care compounds, pharmaceuticals including hormones, and plasticizers (Ebele et al., 2017). New substances are constantly being developed with unknown fates and effects on the environment, making these compounds deserving special attention. Their production has also increased over the years. For example, in 2003, the annual production of penicillin was $2.8x10^4$ tons amounting 60% of the world total consumption of antibiotics. The annual production of EOC can be higher than $2x10^7$ tons (Richardson et al., 2005). Moreover, this production still increases due to the high demands of EOC in preventing or curing disease and sustaining the development of economic such as aquaculture and livestock farming. Consequently, environmental pollution caused by extensive application of EOC is becoming more and more serious.

1.2.1. EOC in WWTP

The main source of EOC occurrence in the environment are the wastewater treatment plants (WWTPs) that can eliminate or remove a substantial amount of these compounds, but there may still be significant concentrations of them in effluents discharged into surface water bodies (Verlicchi et al., 2012; Petrie et al., 2014; de Jesus Gaffney et al., 2017).

The monitoring data on the occurrence of numerous EOC in the influents and treated effluents of WWTPs have been documented over the last two decades worldwide e.g. (Boyd et al., 2003; Ebele et al., 2017; Heberer, 2002a; Richardson et al., 2005).

WWTPs were primarily designed to serve the purpose of removing pathogens, suspended solids and gross organic and inorganic matter, rather than the removal of the increasing numbers of chemicals (e.g. pharmaceuticals and personal care products). Even though EOC are usually found in the aquatic environment at trace concentrations (i.e., between ng L^{-1} and µg L^{-1} or even lower, known as

micropollutants), concerns are rising associated with antimicrobial resistance (Piña et al., 2018) and chronic impacts on biodiversity including endocrine disrupting effects on fish (Meador et al., 2016). Other environmental effects of EOC can be found summarized in (Gogoi et al., 2018).

The recent investigations have examined EOC fate during wastewater treatment, focusing on their removal during conventional (e.g., activated sludge) and advanced (e.g., ozonation and membrane filtration) treatment processes. The results suggest that more studies in EOC remediation should be led to fill the knowledge gaps (Gogoi et al., 2018).

1.2.2. Effluent reuse in agriculture

Over the past thirty years, droughts have dramatically increased in number and intensity in the European Union (EU) and at least 11% of the European population and 17% of its territory have been affected by water scarcity to date (European Comission, 2018).

In order to reduce the demand on water supplies, the effluent from WWTPs have been extensively reused for various purposes in many regions of the world, including landscape and agricultural irrigation (Prosser and Sibley, 2015).

Agriculture plays a key role and a huge responsibility in the potential degradation of natural resources due to the geographical extension, with 50% of the territory by farmland in European Union (Mitchell et al., 2010) and globally makes use of 70% of the available freshwater (FAO, 2018). Without improved efficiency measures and due to increase of population, agricultural water consumption is expected to increase by about 20% globally by 2050 (UN, 2016).

The volume of wastewater generated by domestic, industrial and commercial sources has been increasing along with population, urbanization, improved living conditions, and economic development (Qadir et al., 2010). At present, about 1 billion cubic meters of treated urban wastewater is reused annually, which accounts for approximately 2.4% of the treated urban wastewater effluents and less than 0.5% of annual EU freshwater withdrawals. Recently, the European Commission (EC) proposed on May 2018 new rules to stimulate and facilitate water reuse in the EU for agricultural irrigation (European Comission, 2018). The Regulation proposed by the Commission aims to alleviating water scarcity across the EU. It will ensure that treated wastewater intended for agricultural irrigation is safe, protecting citizens and the environment. The proposal is part of the Commission's 2018 Work Programme, following up on the Circular Economy Action Plan, and completes the existing EU legal framework on water and foodstuffs.

However, the reuse of treated wastewater for irrigation can be a real problem as EOC may transfer to soil potentially increasing the risk to human health upon consumption as they are not regulated and can be accumulated within crop plants (Ben Mordechay et al., 2018; Biel-Maeso et al., 2018; Careghini et al., 2015; Christou et al., 2017; Hurtado et al., 2017). For example, a recent study (Paltiel et al., 2016) shows that human exposure to pharmaceuticals (carbamazepine; an anti-epileptic drug commonly detected in effluents) occurs through the ingestion of commercially available vegetables and fruits

grown in soils irrigated with reclaimed wastewater. Also, diclofenac, caffeine, ibuprofen were found in irrigation water using for crops, and also several of these compounds were afterwards found in the plants (Calderón-Preciado et al., 2011). Malchi et al. (2014) (Malchi et al., 2014) found 14 different EOC, such as carbamazepine, caffeine, clofibric acid, diclofenac, ibuprofen, ketoprofen and naproxen in carrots and sweet potatoes irrigated with treated wastewater. Calderón-Preciado et al. (2011) (Calderón-Preciado et al., 2011) also reported the occurrence of a wide range of EOC e.g. salicylic acid, CAF, ibuprofen, methyl dihydrojasmonate and galaxolide, in apple tree leaves and alfalfa with concentrations of 0.016-16.9 ng g^{-1} (wet weight). Wu et al. (2015) (X. Wu et al., 2015) detected caffeine, carbamazepine, naproxen and triclosan in eight vegetables, with a total EOC concentration in the range of 0.01-3.87 ng g^{-1} (dry weight). The health disorders most frequently associated with the exposure to these contaminants mainly include the development of resistance to pathogens and endocrine disruption, even at very low concentrations (Cunha et al., 2017; Rosal et al., 2010).

1.3. Phosphorus

Phosphorus (P) is essential for all life on the planet. It is vital to the structure of genetic building blocks (DNA and RNA), the production of cell membranes, energy supply, the formation of seeds and fruit in plants and many other biological processes (European Comission, 2013).

Nevertheless, current P use practices are accompanied by various environmental concerns and there is uncertainty about P sustainability in the future. Phosphorus input into croplands is expected to increase 51–86% by the year 2050 (Mogollón et al., 2018). The EU is almost totally dependent on imported phosphate for food and agricultural production. The reserves of P are 85 to 90% controlled by Moroco, China, Algeria, Syria and Jordan processes (European Comission, 2013). The imbalanced distribution of P could cause geopolitical problems for European governments and companies, comparable to the geopolitical tension around fossil energy dependency (e.g. gas, oil and coal). About 90% of mined P is used to produce food and animal feed. Due to dependence on mineral fertilizers for food production and with population rise the reserves of P around the world are decreasing and there is uncertainty about P sustainability in the future (European Comission, 2013).

Humans require approximately 1.2 g of P *per* day, amounting to 3 million tonnes *per* year for global population, which almost 100% of the P consumed in food is excreted in urine (70%) and faeces (30%) (Cordell et al., 2009). Around five times as much as this amount is mined every year to produce mineral fertilizers (Cordell et al., 2012). Today, excreta often end up in waterways via wastewater or as sludge in landfills. In global terms, only a small amount of human excreta is actually treated. Notably, water reuse can be combined with nutrient reuse, particularly P, which are of obvious importance for agricultural production. In WWTP at least one chemical precipitant is added to precipitate the dissolved phosphate into solid phosphates and separating the solid phosphates from the treated wastewater to recover the phosphates. Nevertheless, the reuse of effluent in agriculture could also reduce the use of additional fertilizers, as phosphorus, resulting in savings for the environment and

wastewater treatment (European Comission, 2018). The desired relationship between agriculture and the environment is merged in the expression "sustainable agriculture".

Finally, at the same time, there is also excess P in nature, causing eutrophication and thereby reducing water quality and biodiversity (European Comission, 2013). The benefit of P recovery in WWTP will also contribute to reduce the potential of water eutrophication.

The attempt to remove/recover P from WWTP has had increasingly attention in the last few years. Figure 1.2 shows the evolution of the number of patents over the last 10 years in different countries regarding its recycle or reuse in water. This indicates that the scientific community considers P problematic a challenge that have been research from a range of different and important perspectives, e.g. chemical precipitation, biological processes or adsorption are examples of applied technologies for P removal (Cornel and Schaum, 2009). The electro-based technologies have already shown the possibility of P recovery in WWTP with fresh sewage sludge (Guedes et al., 2015), incineration (Guedes et al., 2014a) and gasification sewage sludge ash (Parés Viader et al., 2017b), and also wastewater focus on simultaneous metals removals (Ebbers et al., 2015). However, the possibility of P reuse/recover from treated wastewater by electro-based technologies with simultaneous removal of EOC was never assessed.

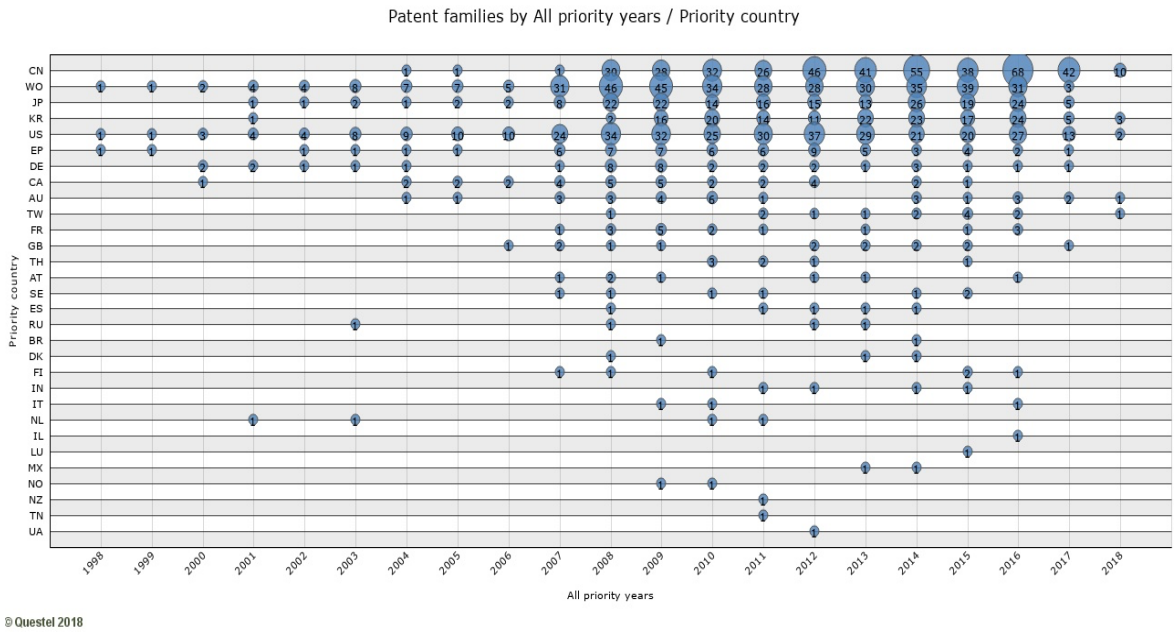


Figure 1.2 - Number of patents worldwide per year from 1998 to 2018 regarding phosphorus in water. (Source: Orbit patents database; CODE: [Phosphor+ AND (water or liquid+ or solution) AND (treatment or recycle or reuse)] OR (water treatment AND P)].

1.4. Remediation technologies

1.4.1. Electro-based technologies

1.4.1.1. Principles overview

The electrokinetic (EK) process is based on the application of a low-level current intensity (direct or alternate), which mobilizes contaminants through three main transport mechanisms: electromigration, electroosmosis and electrophoresis (Acar, Y. B., & Alshawabkeh, 1993; Acar et al., 1993):

- **electromigration** is the movement of ions towards the electrode of opposite charge, being the main transport mechanism for soluble charged species where zeta potential may be small or even absent. Negative ions will move towards the anode whereas positive ions move towards the cathode;
- **electroosmosis** is the movement of pore fluid which generally takes place from the anode to the cathode because the species in the diffusive double layer are often positively charged. It can be from cathode to anode when electrolyte concentration is high, and the pH of pore fluid is low reversing the polarity of the surface charge;
- **electrophoresis** is the transport of charged particles that are attracted electrostatically to one of the electrodes and repelled from the other.

Electroosmosis is the major transport process for non-polar organic compounds, while electromigration is the dominant transport mechanism for ionic compounds. These two processes govern the overall contaminant migration in compact soil systems, whereas the role of the electrophoresis is often negligible, but is relevant in unconsolidated soils (slurries) (Reddy, 2013).

EK treatment relies on several interacting mechanisms but, when using inert electrodes, the dominant and most important electron transfer reactions that occur is the electrolysis of water. As a result of the induced electric potential, electrolysis of water occurs at the electrodes, involving reduction at the cathode and oxidation at the anode (Acar, Y. B., & Alshawabkeh, 1993):

Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Cathode: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

Due to the formation of hydrogen ions in the anode, an acid front is carried towards the cathode. Consequently, there is a pH decrease near the anode and, at the same time, an increase in the pH near the cathode due to the formation of hydroxide ions. The development of an acid and basic front can have significant effects on the magnitude of electroosmosis, as well as, on contaminants removal (Ribeiro et al., 2005).

The EK process has been extensively studied since the late 1980s at the Technical University of Denmark (DTU) and was patented in 1995 (PCT/DK95/00209) as a technique for the restoration of contaminated sites. The original cell design consisted in three compartments (3C; a central compartment containing the contaminated matrix and two end compartments in which electrolytes are circulated and the electrodes are placed). A schematic representation of EK cell can be seen in

Figure 1.3. A new development in EK remediation is the two compartments *set-up* (2C) also developed at Technical University of Denmark (DTU) and patented in 2015 (PCT/EP2014/068956).

The compartments can be separated by passive or ion exchange membranes. Electrodialytic (ED) process was developed for contaminants removal from waste matrices, which differs from EK remediation in the use of ion exchange membranes (IEM) for separation of the waste matrices and solution in the electrode compartments. Between the anode and the polluted matrices an anion exchange membrane (AEM) is applied, allowing the transport of anions out of the central compartment into the anode compartment and preventing the transport of cations across the membrane. A cation exchange membrane (CEM) separates the polluted soil from the cathode, allowing the transport of cations out of the central compartment into the cathode compartment and preventing the transport of anions across the membrane (Ottosen et al., 1997). This prevents transport of ions from the electrolytes through the polluted soil; if, for instance, $NaNO_3$ is used as electrolyte, the ion exchange membranes hinder the transport of Na^+ and NO^-_3. The application of ion exchange membranes avoids formation of acidic and alkaline fronts by H^+ and OH^- generated in the electrolysis reactions at the electrodes.

The EK/ED remediation is fairly simple to implement and operate, but the fundamental reactions that govern the remediation method are complex. Under an induced electric potential, the successful implementation of the remediation process requires the understanding of the electrochemical processes, transport mechanisms and physico-chemical processes that affect the fate of contaminants, being essential in order to optimize the system performance.

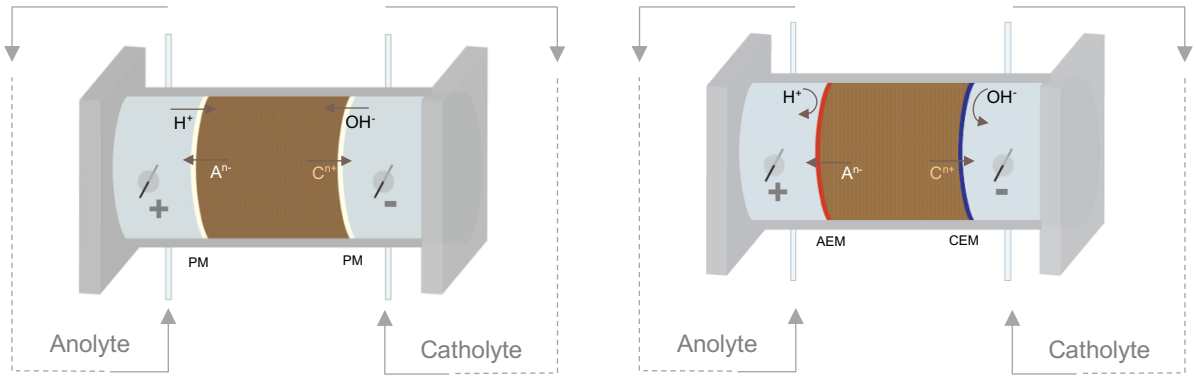


Figure 1.3 - Schematic representation of a 3-compartments (a) electrokinetic (using passive membranes) and (b) electrodialytic cell (using anion and cation exchange membranes (AEM and CEM).

EK process was originally applied in situ for heavy metals removal from consolidated soil (e.g. chromium, cadmium, copper, uranium, mercury and zinc) (Ottosen et al., 1997), but the process was quickly expanded to be used ex-situ and with other type of contaminants: polycyclic aromatic hydrocarbons (Lima et al., 2012), polychlorinated biphenyls (Gomes et al., 2014), atrazine (Ribeiro et al., 2005), molinate and bentazone (Ribeiro et al., 2011). Along with different types of contaminants, different matrices such as saturated (Ottosen et al., 1997) and unsaturated soils (Ribeiro et al., 2011),

wood waste (Ottosen et al., 2009a), sewage sludge ash (Guedes et al., 2014a; Parés Viader et al., 2017b), sediments (Colacicco et al., 2010), mine tailings (Kim et al., 2005) and membrane concentrate (Couto et al. 2013; Couto et al. 2015) have been successfully tested.

1.4.1.2. Electro-based technologies for soil remediation

Soil pollution is still an unsolved problem despite the efforts spent during the last two decades in research and development of innovative soil remediation technologies. Soil remediation is at the cutting edge of environmental technology as pollution of soils is currently an environmental issue of major significance. Soil remediation is considered a difficult task due to several factors e.g. chemical composition of soil, nature of contaminants, interaction of contaminants and soil, aging of contaminants (Reddy, 2013). Thus, so far, there is not a general technology that can work as general solution for soil contamination, with satisfactory results for the remediation of any soil or any contaminant. Soil remediation technologies tend to be site-specific and the success of the remediation in a contaminated site do not assure satisfactory results in other sites.

The EPA has documented inadequate performance of various remediation technologies (Usepa, 2000) which may be attributed to (1) matrix characteristic; (2) heterogeneous conditions of the site (e.g. clayey within sand formation); (3) physical and chemical characteristics of the contaminants (e.g. hydrophobic organic contaminants can be difficult to remove); (4) co-existing inorganic and organic contamination (Maturi and Reddy, 2006).

In the development of the soil remediation technology, some factors should be considered (i) avoid the rapid diffusion of pollution after an accidental discharge event, and (ii) avoid substantial modification in soil properties resulting from pollutants removal.

In general, all the remediation technologies have drawbacks e.g. high costs, change of soil characteristics, low efficiency, long treatment time requirements or selectivity towards target pollutants. The advantages and limitations of the EK process are shown in Table 1.1. This technique is considered a simple method that can be applied in several contaminated environments and conditions with low costs comparing with other remediation technologies. The process is particularly effective for fine grained porous media, in small periods of time, and allows the separation of compounds towards one of the electrodes. The process can be applied *in situ* or *ex situ* and be combined with other remediation technologies e.g. with phytotechnologies (Cameselle et al., 2013; Nazaré Couto et al., 2015). Like all the techniques, EK also has his own drawbacks, including the limited desorption of some contaminants from the matrices being necessary sometimes to apply chemicals to enhance the removals (Ottosen et al., 2000; Saichek and Reddy, 2005). Also, the different characteristics of each site, especially if the geology and the hydrology of the contaminated site are different from one location to another one, has influence in contaminants removal rates.

Table 1.1 - Advantages and limitations of electrokinetic process in soil (adapted from (Virkutyte et al., 2002)).

Advantages	Limitations
In situ and *ex situ* technology	Limited by contaminant desorption
Allows the simultaneous removal of inorganic and organic compounds	Acid or alkaline conditions may create difficulties in remediation
Use of the pH produced by the electrolysis of water to effectively desorb contaminating ions	Precipitation of species close to the electrode
Potentially effective in different kinds of matrices	Sometimes need to apply enhancing solutions
Competitive in terms of cost-effectiveness	Removal efficiency can be affected by large rocks or gravel present in soil
Can be used to enhance other remediation methodologies like bioremediation	Water present in soil can limit the electro-osmotic flow

For heavy metals and metalloids removal, many researches have been conducted to allow the rehabilitation of contaminated soil, e.g. oxidation (Mondal et al., 2013), phytoremediation (Nazaré Couto et al., 2015), soil washing (Cao et al., 2016; Im et al., 2015; Kumpiene et al., 2017) and electrokinetics (Kim et al. 2005).

Contrary to organic substances, metals and metalloids cannot be degraded. Hence, the options are either to separate contaminants from soil, or make them less soluble, i.e. immobilize them within the soil through chemical stabilization (Kumpiene et al., 2008).

Among remediation technologies to separate the contaminants from soil, EK/ED soil remediation have been shown to be effective for metals and metalloids removals e.g. (Christensen et al., 2006; W. S. Kim et al., 2005; Ricart et al., 2008). In order to overcome the removal difficulties, several chemicals have been used as extracting agents in order to enhance the desorption of soil pollutants. For example, the ED remediation success in an un-enhanced 3-compartment electrodialytic cell was reported limited, e.g. 35% of As removal was obtained from a Danish soil , and by mixing ammonia into the soil, the removal improved and As was reduced from 900 mg kg^{-1} to 90 mg kg^{-1} in some parts of the Danish soil (Ottosen et al. 2009). Ammonia causes the soil to be alkaline and As is mainly present as negatively charged species in the alkaline environment and thus As is mobile in the electric field. Based on literature assessment, even with the knowledge established by years of research, the scientific understanding of As removal using EK/ED is continuously evolving. The As removal have been tested by various techniques in solid and liquid matrices, e.g.: oxidation and filtration, photochemical oxidation, biological oxidation, phytoremediation, electrocoagulation, membrane technology (Singh et al. 2015), but the results are dependent of specific conditions, e.g. soil characteristics (Arco-Lázaro et al., 2016; Soil et al., 2007) and pH conditions (Baek et al., 2009; Ryu et al., 2011).

For organic contaminants, soil remediation by EK/ED has been showing to be a promising technology for a different range of compounds e.g. polycyclic aromatic hydrocarbon (PAH) (Pazos et al., 2010) and

polychlorinated biphenyl (PCB) (Gomes et al., 2015), but regarding the EOC removal in soil by EK, only few studies were found to test it (Guedes et al., 2014b). Results showed that EK is a viable method for the remediation of these contaminants both through mobilization by electroosmotic flow and by electrodegradation. As electroosmotic flow is very sensible to soil pH, pH control in the anolyte increased electroosmotic flow rate, consequently enhancing contaminants mobilization towards the cathode end. The extent of the mobilization towards the electrode end was mainly dependent on compounds solubility and octanol-water partition coefficient.

1.4.1.3. Electro-based technologies for effluent treatment

The treatment of urban wastewater is one of the biggest challenges of the twenty-first century. The worldwide fresh water scarcity is increasing the demand for non-conventional water resources as the management of water goes by effluent reuse.

The recent investigations have examined EOC fate during wastewater treatment, focusing on their removal during conventional (e.g., activated sludge) and advanced (e.g., ozonation and membrane filtration) treatment processes. It is suggested that more exhaustive studies be led to fill knowledge gaps in the conduct of EOC under traditional sewage treatment and advanced treatment techniques (Gogoi et al., 2018). There are advanced treatment processes, such as activated carbon adsorption, advanced oxidation processes, nanofiltration, reverse osmosis, and membrane bioreactors that can achieve high removals of contaminants removal (Luo et al., 2014). However, the application of such technologies implies a high cost in water treatment. In addition, sometimes, these technologies do not achieve a complete mineralization of the contaminant leading sometimes to secondary pollution (Martínez-Huitle and Ferro, 2006).

Research efforts are underway to develop more powerful oxidation methods than those currently applied in WWTP for achieving the complete destruction of EOC, but so far, successful mitigation strategies have not yet been established (Schröder et al., 2016). Therefore, the search for alternative techniques is necessary to improve degradation of organic contaminants (parent and secondary metabolites) and reduce the costs associated with effluent treatment in WWTP allowing its safe reuse (Luo et al., 2014). In this context, several electrochemical advanced oxidation processes (EAOPs) are being currently developed for wastewater treatment (Gupta et al., 2012). The electrochemical methods for wastewater treatment offer a great advantage, since no additional chemicals are required as e.g. in electro-Fenton oxidation (Chu et al., 2012), and the electron may be considered as a “green,” controllable reagent. The number of publications with EOC, as pharmaceuticals and personal care products (PPCPs), in wastewater or effluent, as well as, with electro-technologies have been increasing over the years, which shows the interest for these compounds (Figure 1.4).

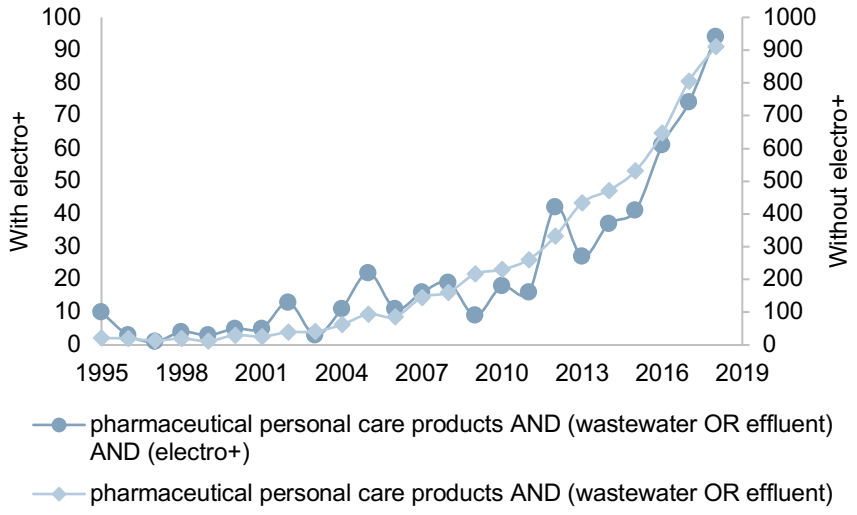
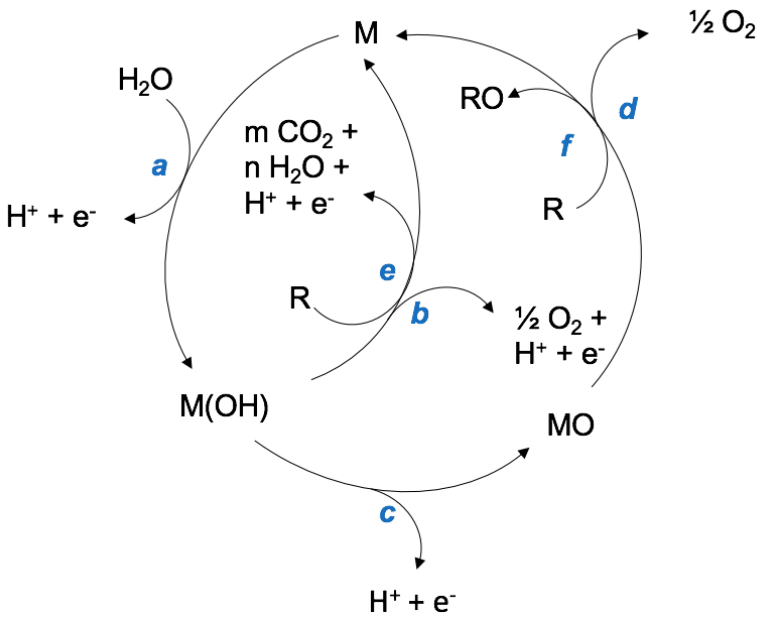


Figure 1.4 - Publications over the time regarding EOC as PPCPs in wastewater or effluent.

The great effectiveness of electrochemical methods is due to the production of hydroxyl radical (•OH), which is a non-selective, very powerful oxidizing agent (2.8 V) able to react with organics giving dehydrogenated or hydroxylated derivatives, up to their complete mineralization is reached (conversion into CO_2, water and inorganic ions) (Tung et al., 2013).

The electrochemical oxidation of organic pollutants can take place in two ways depending on the electrode surface: (i) direct electron exchange between the contaminant and the electrode surface, or (ii) by indirect *in situ* electro generation of catalytic species, which are able to promote contaminant oxidation with their high oxidizing power (Wu et al. 2014). The effectiveness of anodic oxidation for wastewater treatment depends largely upon the properties of the anodes material and the organic substances involved in the process (Cui et al., 2009; Feng et al., 2014; Li et al., 2005). The complete destruction of the organic substrate or its selective conversion into oxidation products is schematically represented in Figure 1.5, that assumes the existence of ‘‘active’’ and ‘‘non-active’’ anodes. Both kinds of anodes (M) oxidize the water forming the physiosorbed hydroxyl radical (M(•OH)). This radical interacts strongly with the surface of the ‘‘active’’ anodes, being transformed into the chemisorbed “active oxygen” or superoxide MO, with the MO/M pair being a mediator in the electrochemical conversion of organic compounds; the surface of “non-active oxygen” anodes interact weakly with M(•OH) and this radical directly reacts with organics until total mineralization is achieved. In generak, weak (M(•OH)) interactions lead to low anode activity toward oxygen evolution (high overvoltage anodes) and high is the anode reactivity for organics oxidation (fast chemical reaction) (Comninellis, 1994). Ruthenium dioxide, iridium dioxide, platinum, graphite are typical examples of “active anodes”, while lead dioxide, tin dioxide, BDD and sub-stoichiometric TiO_2 electrodes can be considered as “non-active” electrodes, with the BDD anode being the most potent “non-active” anode known (Feier et al., 2018; Rivera-Utrilla et al., 2013).



Legend:
(a) Formation of hydroxyl radicals, OH;
(b) oxygen evolution by electrochemical oxidation of hydroxyl radicals;
(c) formation of the higher metal oxide, MO;
(d) oxygen evolution by chemical decomposition of the higher metal oxide;
(e) electrochemical combustion of the organic compound via hydroxyl radicals;
(f) electrochemical conversion of the organic compound, R, via the higher metal oxide.

Figure 1.5 - Mechanistic scheme of anodic oxidation of organic compounds with simultaneous oxygen evolution on non-active anodes (reactions a, b and e) and active anodes (reactions a, c, d and f). (Source: Comninellis, 1994).

1.4.2. Constructed wetlands

The constructed wetlands (CWs) are designed to mimic the process involved in natural wetland systems, but within a more controlled environment (Wu et al., 2015). Physico-chemical properties of wetlands provide many positive attributes for contaminants removal (Williams, 2002). The removal efficiency in CWs is attributed to the coexistence of different microenvironments (plants, substrate, and associated microbial assemblages), which leads to a variety of parallel pathways for contaminants degradation. In WWTPs, in contrast, the physicochemical conditions tend to be more homogenous (without these dynamic interactions), limiting the number of degradation pathways that exist (Hijosa-Valsero et al., 2010). In Figure 1.6 is shown the main removal mechanisms in CWs (Zhang et al., 2013).

CWs has been widely used to treat various kinds of wastewaters (Vymazal, 2009), such as domestic (Yang et al., 2007), agricultural (Dordio and Carvalho, 2013) and industrial wastewater (Wu et al., 2015), but also storm water and acid mine drainage (Nyquist and Greger, 2009). The applicability of CWs for the remediation of EOC has been increasingly explored and proved to be successful for a variety of compounds with a simultaneous improvement of water quality (Ávila et al., 2014; Carvalho et al., 2013; Dordio et al., 2010; Matamoros et al., 2009, 2008; Matamoros and Bayona, 2006). However, the physico-chemical processes contributing to contaminants degradation have not been thoroughly

described and it is imperative to understand the drivers of EOC removal, aiming to optimize CWs design for an effective contaminant removal (Hijosa-Valsero et al., 2010).

The treatment performance in CWs is critically dependent on the optimal operating parameters and includes water depth, hydraulic load, hydraulic retention time and feeding mode related to the sustainable operation for wastewater treatments (Wu et al., 2015). CWs can be classified according to their hydrology (free water surface, subsurface flow and hybrid), flow path (horizontal or vertical) and types of macrophyte (free-floating, emergent and submerged) (Li et al., 2013). According to Zhang et al. (2014) (Zhang et al., 2014a) horizontal subsurface flow CWs have been the most frequently employed aquatic plant-based systems to remove pharmaceutical compounds, although vertical subsurface flow CWs and hybrid CWs have also shown good removal efficiencies.

The advantages of CWs include a cost benefit (e.g., lower energy requirement and operating costs), benefit landscape and represent a significant wildlife habitat. The broad application of CWs may be limited by land requirement (especially in regions where land resources are scarce and population density is high), the presence of toxic chemicals influencing biological components (e.g. ammonia and pesticides) and the temporal decrease of treatment effectiveness due to the peaks of contaminants in water flow. CWs typically have longer hydraulic retention times than conventional treatment systems. This restricts their use to situations where a large footprint can be accommodated or where the wastewater volume is small. CWs represent an option that fits the purposes of a green treatment technology with low operation and maintenance requirements (Wu et al., 2015). They are part of the tertiary treatment from WWTPs and may be assumed as a polishing step before discharge into the aquatic bodies.

The role of plants in CWs have been frequently discussed and several studies state their crucial role, being considered as an essential component of the design of CW treatments (Zhang et al., 2014). The roots maintain the hydraulic properties of the substrate and the shoots protect the surface from erosion while shading prevents algae growth. Besides, plants play another important role in stimulating the development and activities of microbial populations, which are supported by the rhizodeposition products (i.e., exudates) promoting the occurrence of various biological processes in the rhizosphere (e.g., transformation and mineralization of nutrients and organic pollutants) (Stottmeister et al., 2003).

The soil matrix is also important in CWs, because provides a suitable growth medium for plant and microorganisms together with a successful movement of wastewater (Calheiros et al., 2008). The frequently used substrates include natural (sand, gravel, clay), artificial (light weight aggregates, actived carbon) and industrial (slag) materials (Wu et al., 2015). Substrates can remove contaminants from wastewater by exchange, adsorption, precipitation and complexation (Dordio et al., 2010). For this reason the chosen materials are extremely important when designing CWs as, e.g., a material with high sorption capacity will improve contaminants removal (Zhang et al., 2013).

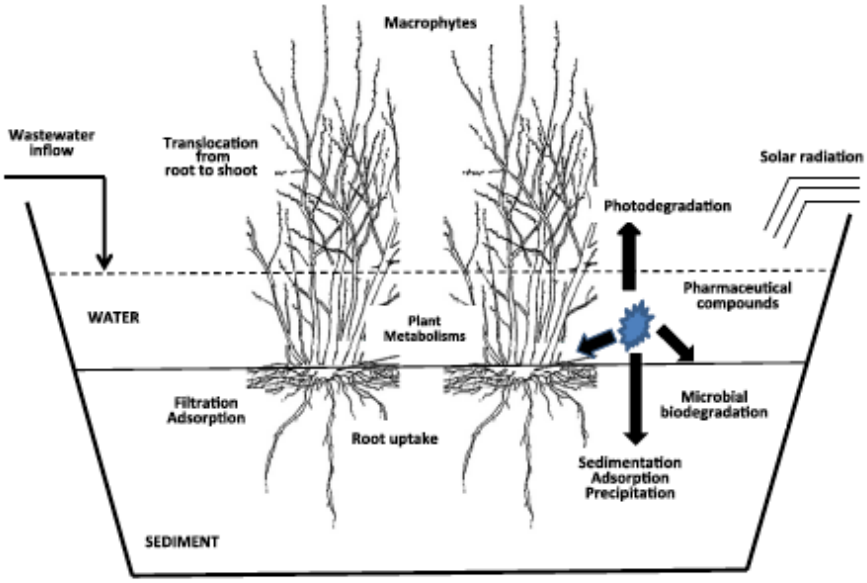


Figure 1.6 - Mechanisms of removal in CWs. (Source: Zhang et al., 2013).

1.5. Motivation and objectives

The present work is part of the INTERREG SUDOE project *4KET4REUSE - KETs for the removal of emerging contaminants in treated wastewater from the SUDOE area*, (SOE1/P1/E0253; 2016 – 2019), whose main objective is to promote innovative capabilities for a sustainable growth by decreasing concentration of target contaminants in effluent for a safer discharge to the receiving water bodies and/or to promote a safer water re-use in agriculture, and consequently in agricultural soil.

The main research objective of this Ph.D. work was to investigate and optimize an effective integrated treatment strategy, using electro-based technologies, for EOC removal either from soil or effluent. Thus, this Ph.D. focused on the downstream and upstream remediation from the contamination source.

The study of soil contamination legacy targeted the downstream source of the problem aiming to remediate contaminants that are resistant to soil natural attenuation (self-depuration capacity of the system), in short periods of time without causing soil disturbances. Arsenic (a mobile and toxic metalloid) was chosen due to its widespread use, soil persistence, crop uptake potential and public health risk. Hydrocarbons were selected due to the frequency of the oil spills being considered one of the main soil pollutants.

The effluent contamination by EOC is focused on the upstream source of the problem, taking a preventive strategy. In this sense, a tertiary step would be introduced as a polishing step in WWTPs. The application of an efficient electro-technology depends on several variables including matrix characteristics and contaminants properties therefore, a deeper understanding of the mechanisms/parameters underlying the proposed technique was carried out.

The scientific purpose of this work follows the circular economy principle (Figure 1.7) in a way that promotes a safe agricultural reuse of effluent (water management), avoiding future soil (and potential

crop) contamination, and a safe discharge into the aquatic environment. In addition, effluent reuse in agriculture contributes to nutrients recycling, as phosphorus, alleviating pressure on over-exploited resources (e.g. phosphate rock, included in the EU list of 27 Critical Raw Materials; (European Commission, 2017)).

The use of electro-based technologies to remediate contaminated matrices is thus, of great interest to public and the environmental health as it presents itself as a versatile and promising technology with potential for reducing the environmental and human risks associated with the spread of contamination.

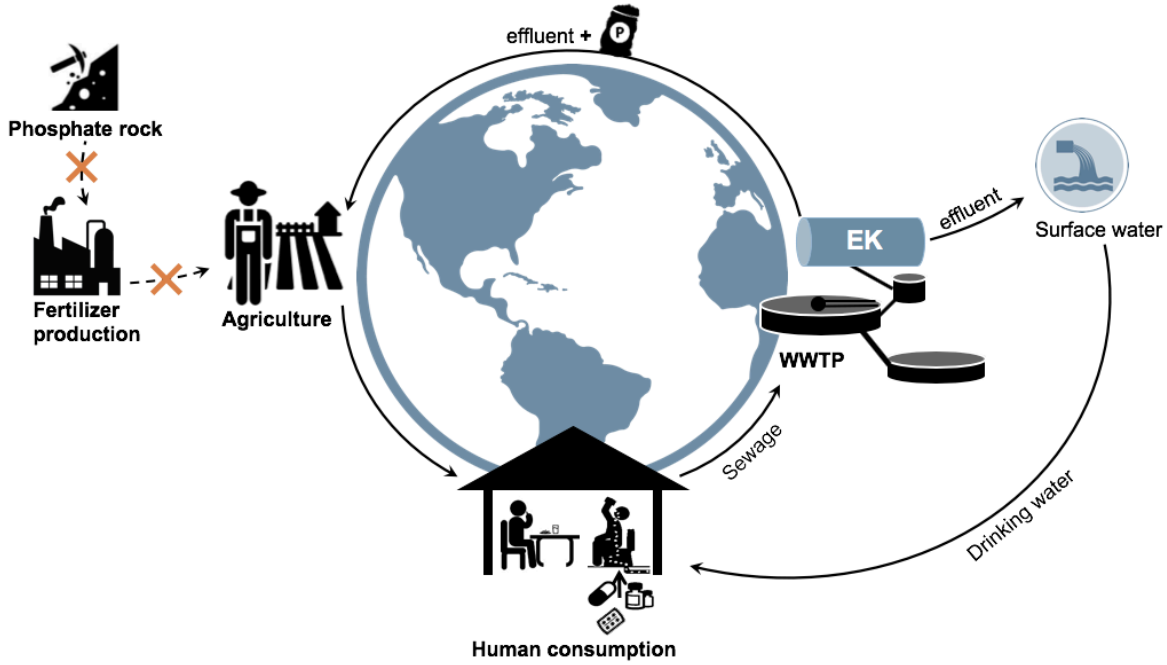


Figure 1.7 – Circular economy principle applied to the Ph.D. work.

1.5.1. Study objects background

The following studies were conducted in order to fulfil the Ph.D. objectives:

1.5.1.1. Arsenic removal from soil

The remediation of a soil highly polluted with As from wood preservation industry by electrodialytic remediation (EDR) was the focus of this work. A 2-compartment (2C) electrodialytic cell design with soil suspension either in the anode or cathode compartment together with pH adjustment (alkaline in anolyte and acid in catholyte) was tested. With the best 2C-cell set-up from the two designs previously tested, the comparison between (i) original soil, (ii) washed soil and (iii) fine fraction (washing process combined with sieving) was made. The aim was to test the feasibility of combining soil washing with

EDR by comparing it without prewashing, in order to asses any potential enhancement in As remediation.

The potential reuse of treated soil was also studied for building materials.

1.5.1.2. Petroleum hydrocarbons removal from soil

The aim of this work was to develop an electrokinetic remediation (EKR) strategy for oil-polluted soil that could work as an effective remediation technology that required minimum maintenance and entailed less soil disturbance. For that, the feasibility of different current strategies was assessed: reversed electrode polarization (REP) and switching the current On/Off. The work was carried out with soil collected in Sisimiut, Greenland from a dump site after an oil spill. The Arctic environment is very fragile to anthropogenic disturbances and the study of *in situ* remediation technologies that can be used to avoid the rapid diffusion of pollution after an accidental oil spill is therefore an important tool. The influence of cold temperature (6 ºC) in oil remediation was compared with experiments made at room temperature (22 ºC).

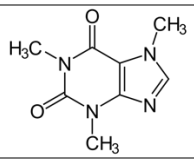
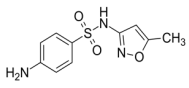
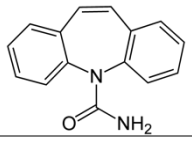
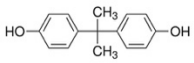
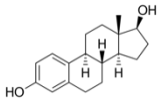
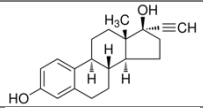
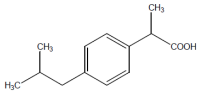
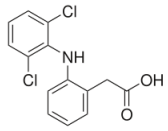
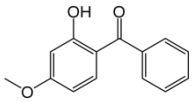
1.5.1.3. Emerging organic contaminants removal

Nine different EOC were selected for this Ph.D. work: caffeine (CAF), sulfamethoxazole (SFM), carbamazepine (CBMP), bisphenol A (BPA), 17α- ethinyloestradiol (EE2), 17β-oestradiol (E2), ibuprofen (Ibu), diclofenac (DCF) and oxybenzone (2-hydroxy-4-methoxybenzophenone, MBPh).

The EOC selection was based on their frequency in the effluent, being four of them in common among Portugal, Spain and France (the list where the information was crossed can be seen in Appendix 1). The four EOC in common were: SFM, CBMP, DCF and IBF. Moreover, the estrogens (E2, EE2) are in the EU Watch list (Decision 2015/495/EU), MBPh represent a seasonal contaminant (Tsui et al., 2014), CAF and BPA are well known due to their widespread use and consume of products containing these compounds.

In addition to the aforementioned reasons, all of the EOC present different physico-chemical characteristics (e.g. solubility, octanol-water partition coefficient; Table 1.2) in order to have a representative study in EOC removal.

Table 1.2 - Chemical structure and properties of the emerging organic contaminants.

Compound	Chemical structure	Formula	MW (g mol^{-1})	Log K_{ow} [a]	pKa [b]	Sol. in water (mg L^{-1})	UV abs (nm)	Category
Caffeine (CAF)		$C_8H_{10}N_4O_2$	194.19	-0.07	14.0 [c]	2.16×10^{4} [d]	273	Central nervous system stimulant
Sulfamethoxazole (SFM)		$C_{10}H_{11}N_3O_3S$	253.279	0.89	5.7	610 [f]	268	Antibiotic
Carbamazepine (CBMP)		$C_{15}H_{12}N_2O$	236.274	2.45	13.9	18 [d]	284	Anticonvulsive
Bisphenol A (BPA)		$C_{15}H_{16}O_2$	228.29	3.32	9.6-11.3	120 [d]	277.1	Plasticizer
17β-oestradiol (E2)		$C_{18}H_{24}O_2$	272.38	4.01	10.7	3.90 [e]	280	Estrogen
17α-ethinylestradiol (EE2)		$C_{20}H_{24}O_2$	296.40	3.67	10.3	11.3 [e]	280	Estrogen
Ibuprofen (IBU)		$C_{13}H_{18}O_2$	206.19	3.97	4.91	21 [d]	220	Anti-inflammatory
Diclofenac (DCF)		$C_{14}H_{11}Cl_2NO_2$	296.147	4.51	4.15	2.37 [d]	276	Anti-inflammatory
Oxybenzone (MBPh)		$C_{14}H_{12}O_3$	228.25	3.82	7.56	69 [d]	288/329	UV filter

References: http://pubchem.ncbi.nlm.nih.gov/, www.chemicalbook.com, www.SigmaAldrich.com.
Legend:
[a] logarithm of the octanol- water partition coefficient; [b] logarithm of acid dissociation constant:
[c] at 40 ◦C
[d] at 25 ◦C
[e] at 27 ◦C
[f] at 37 °C

1.5.1.3.1. EOC removal from soil

The general goal of this study was to find a remediation solution for EOC associated with effluent irrigation in agricultural soils. The hypothesis of EOC removal by electro-based technologies either ex situ or in situ was studied.

a) Influence of the cell design in EOC removal from soil slurry

The *ex situ* soil remediation was tested with soil suspended in three different cell designs: two ED cells (with 3 and 2 compartments cell; 3C- and 2C-cell, respectively), one electro-chemical cell (1 compartment cell; 1C-cell), and their controls (without electric current). The aim was to study the remediation and/or mobilization of EOC from slurry soil. The target EOC were: BPA, EE2 and MBPh, as they present different physical and chemical characteristics, belonging to different categories and were already detected in various environmental compartments.

b) Electrokinetic as a remediation strategy for soil irrigated with contaminated effluent

The present work was focus on the EOC removal from soil avoiding their diffusion in soil after irrigation with contaminated effluent. The strategy was to develop an EKR treatment that could work as an effective remediation technology with minimum maintenance requirements and soil disturbance. Hence, different current strategies were tested applying a very low current intensity (below 2.5 mA for 300 g of soil).

1.5.1.3.2. EOC removal from effluent

In the study of EOC removal from effluent, different treatments were designed: constructed wetlands (CWs) and electro-based technologies.

a) Simulated constructed wetlands

The aim of the present work was to evaluate the capacity of CWs having LECA as a support medium and planted with the salt marsh plant *Spartina maritima* to remove EOC from wastewater. The target compounds were CAF, MBPh, and TCS, chosen based on their worldwide consumption, physicochemical properties, and chemical classes. The role of each variable: LECA, plant and the possible synergetic effects were assessed. A fed-batch mode was simulated with pulses of contaminants addition throughout the experiment.

b) Electrodialytic 2-compartments cell

The main goal of this work was to develop a cost-effective technology for WWTP where EOC could be removed and phosphorus be recovered having in mind effluent reuse in agriculture. For this, a 2C-cell with four different configurations was tested. The effluent was placed either in anode or cathode compartment, separated from the electrolyte compartment through an anion or a cation exchange membrane (AEM and CEM, respectively). Five EOC were selected: CAF, BPA, E2, EE2 and MBPh.

c) Electrochemical degradation in 1-compartment cell

A vertical and horizontal single-compartment cells were investigated in flow rate and batch mode, respectively. The work aimed to optimize the EOC removal from effluent, regarding operating parameters, as electrodes material and current intensity.

In the vertical EK-reactor, 2 mL min^{-1} of effluent was treated, with six EOC (SFM, CBMP, BPA, EE2, DCF and MBPh), testing two different electrodes materials (graphite and platinized titanium) and current intensities (25 mA and 100 mA).

In the horizontal EK-reactor working in batch mode (2 hours of treatment) nine EOC were considered: CAF, SFM, CBMP, BPA, E2, EE2, DCF, IBF and MBPh. Different anodes, in terms of material and shape were tested with a fixed cathode (titanium bar coated with MMO). The anode materials (MMO containing IrO_2 and RuO_2/Ti and Pt/Ti) were selected based on its expected electro-catalytic function for organic oxidation already known as very stable and due to the acid/alkaline and corrosion resistance. The effect of different current density and influence of cathode on EOC degradation was also assessed.

The proof-of-concept for the EK reactor with optimized conditions (anode, cathode and current intensity) was carried out.

d) Integrated EK/ED treatment with 1C and 2C-cells

This work aimed to assess the potential of electro-based technology for simultaneous removal of EOC removal and P recovery/reuse by the combination of 1C and 2C-cell.

1.6. Original contribution

Multidisciplinary and cross-cutting research was carried out in the present work based on electro-based technologies envisages the promotion of economic, social and environmental benefits.

In order to achieve the goals previously explained, innovative EK/ED set-ups with a deeper understanding about the main variables/mechanisms that affect the process were performed focusing in process optimization. The here present results also contribute for existing knowledge gaps in literature, which can help future researches.

For the removal of legacy contamination by arsenic, petroleum hydrocarbons and the EOC from soil:

- The feasibility of combining a pre-treated soil (washing with flocculant and sieving) in order to enhance the As removal in the ED process was tested for the first time;
- The EK process to clean-up oil spilled on polar soil was studied considering cold temperature. In addition, different current strategies were also tested aiming minimum maintenance and disturbance avoiding the rapid diffusion of pollution after an accidental oil spill;
- Three EK/ED (1, 2 and 3C) cell designs were study for the first time exploring the EOC degradation/mobilization from soil slurry;

- The fate of EOC was rarely investigated after effluent irrigation, with few studies reporting the effect of reclaimed water matrix on EOC fate in soils. Moreover, no studies were found about remediation technologies after soil irrigation with contaminated effluent to assesses EOC mitigation in order to avoid the potential risks. Thus, the feasibility of EK as a remediation technology after effluent irrigation with EOC was assessed for the first time.

For EOC removal from effluent:

- The specie of plant *Spartina maritima* was for the first time considered as a possibility in CWs for EOC removal with LECA as a substrate;
- The effluent treatment by EK/ED had never been explored in WWTPs making it a big and innovative challenge:
    - The ED process was applied for the first time in effluent for simultaneous EOC removal and P recovery/reuse; and the 4 possible 2C-cell combinations were tested;
    - The EK process was optimized testing different operational parameters: flow/batch, vertical/horizontal, time, material and shape of the electrodes;
    - A new EK reactor for EOC removal from effluent was designed and optimized and a patent is envisaged.

1.7. Dissertation outline and content

The Ph.D. thesis was divided in two parts. The first part of the thesis was divided in five sections: the first section consisted in an introductory chapter of the problematic approached in the present work. The Section II presents a synthesis of the experimental approaches implemented to reach the objectives proposed. In Section III the results achieved from the experimental work and the major findings are presented. The last two sections consist in the overall conclusion of the work and future development, Section IV and Section V, respectively.

Part II of the dissertation includes all the publications in peer-reviewed journals (published, submitted and under preparation) that were developed during the Ph.D. study. As Part I is a summary of the publications presented in Part II, some overlap and repetition are inevitable.

SECTION II

2. MATERIALS AND METHODS

2.1. Sampling of matrices

2.1.1. Collstrop soil

Soil was sampled from the top layer at an abandoned wood preservation site, Collstrop site in Hillerød, Denmark. Soil was excavated from a 1 m deep trench and the grass turf was removed before excavation.

Part of the 'original soil' was washed at a German industrial soil washing facility. The washing process consists of a series of mechanical separation steps, which the soil slurry runs through, aiming to separate the coarse fractions from the fine fractions. The process consisted in five steps: i) mechanical separation of the oversized grains with a screen; ii) a second screen to separate out the stones and gravel; iii) a jigger to take out the very light fraction (e.g. grass); iv) coil aggregate, which separates small particles by separation in a cyclone; v) concentrator or filter press, which separates the fine fraction from water. In the washing process, a high molecular weight anionic polyacrylamide flocculant supplied as a liquid dispersion grade (0.2% polymer-based flocculant, Magnafloc 120L from BASF) was added to the closed system of 80 m^3 of recycling water. The anionic polyacrylamide flocculant physically forms inter-particle bridges that draw colloids into larger aggregates, which leads to a faster settling of the fine particles and the possibility to separate them from the water.

The fine fraction was not obtained after washing due to particles aggregation and part of the washed soil was dry-sieved and subjected to automatic shaking in a 0.063 mm sieve positioned in a vibrating screen instrument where the fine fraction was obtained. The sequence of the experimental process for the soil studied is shown in Figure 2.1.

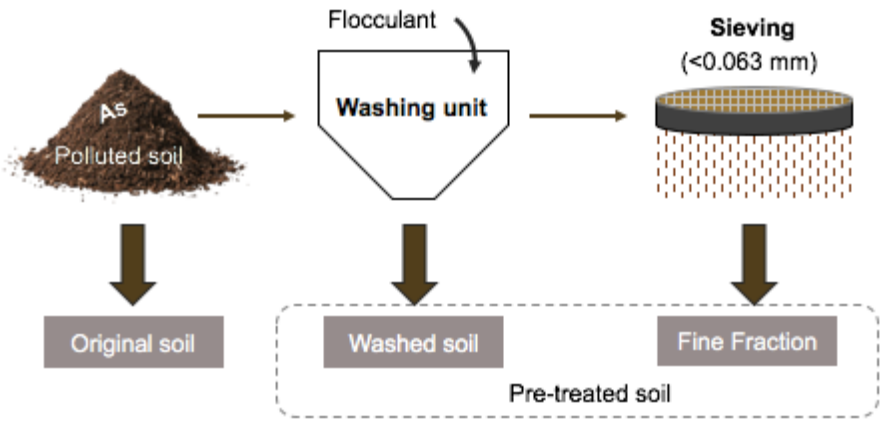


Figure 2.1 - Experimental soil (original, washed and fine fraction) used in ED remediation of As.

2.1.2. Polar soil

The soil samples were taken in Sisimiut dump site where barrels of waste oil are stored prior to incineration at the local waste incineration plant oil spills were visible. The soil in study was sampled from one of the identified spills in August 2017. During the sampling, a strong odour of oil products and free phase oil in the surface was observed. The soil was dug up from 0 to 30 cm depth by using a shovel and transported to Denmark in a polyethylene bucket. In laboratory, the soil was carefully homogenized by turning it continuously and removal of larger particles such as stones, bricks, clinker and fibrous roots.

2.1.3. Agricultural soil

The soil was sampled from *Paul de Magos, Salvaterra de Magos*, Portugal, at 0-20 cm depth, and correspond to a Fluvisols (World Reference Base for Soil). The soil was spiked with EOC before the EK and ED remediation experiments.

2.1.4. Effluent

Effluent samples were collected at a WWTP from *Simarsul* located in *Quinta do Conde, Sesimbra*, Portugal. The WWTP has infrastructures with capacity to treat urban wastewater corresponding to about 94,000 equivalent inhabitants and the level of installed treatment is tertiary (UV light). The WWTP has an aerobic reactor of suspended biomass to allow the biological treatment of wastewater. The effluent from this reactor goes to the secondary settling tank for phase separation where liquid samples were collected. Once at the laboratory, and to remove colloidal particles from the secondary effluent, the samples were pretreated using a 0.45-μm MF filter, and the filtered effluent was used in all experiments.

2.2. Experimental design and conditions

2.2.1. Arsenic removal from soil

The ED experiments performed are summarized in Table 2.1.

A two compartment (2C) cell set-up was tested varying the position of contaminated soil and the electrolyte conditioning with a strong base and a strong acid (see

Figure 2.2 a) and b)). The soil compartment was filled with 50 g of soil and 350 mL of distilled water corresponding a liquid/solid (L/S) ratio of 7. In ED treatment 1 (T1) the suspended soil was kept in the anode compartment, a CEM was used to separate the two compartments and catholyte pH was adjusted to 2 throughout the treatment (Figure 2.2 a)). In ED treatment 2 (T2) the suspended soil was kept at the cathode compartment, an AEM was used to separate compartments, and anolyte pH was adjusted to 10 (Figure 2.2 b)). The experiment without electrolyte conditioning and with suspended soil in cathode was also performed (T2*).

The second part of the work consisted if combining the pre-treated soil soil (washing) with ED process could enhance As removal from soil by. For this, the best 2C-cell set-up previously tested, was used. The soil was termed 'original' if it is not washed, and "floc" when it was washed at the German soil washing plant. The fine fraction obtained after dry-sieved the washed soil "floc" was named as "FF floc".

The ED experiments were carried out in a cylindrical Plexiglas-cells with an internal diameter of 8 cm. The cathode compartment with the soil slurry was 10 cm, whereas the anode compartment was 5 cm long (and *vice-versa* for T2). An overhead stirrer was used to stir the soil slurry. Ion exchange membranes separating the soil compartment from the electrode compartment were from Ionics, anion exchange membrane (AEM, AR204 SZRA B02249C) and cation exchange membrane (CEM, CR67 HUY N12116B). The electrodes were platinized coated titanium bars, with a 3 mm diameter from Permascand®. A power supply (Agilent E3612A) was used to maintain a constant direct current (DC) current. The fresh electrolyte (500 mL in total of 10^{-2} M $NaNO_3$) was circulated in a closed system by a "Pan World" magnetic pumps from Plastomec Magnet pump model P05 between the chamber and a glass bottle. The electrolyte was conditioned at the beginning of the experiment, and whenever necessary, to achieve an acidic (pH=2) or alkaline pH (pH=10), depending on the applied treatment. The pH of the electrolytes was adjusted whenever needed by addition of HNO_3 (1:1) and NaOH (6M). The voltage between working electrodes, conductivity and pH of both cell compartments were measured twice a day.

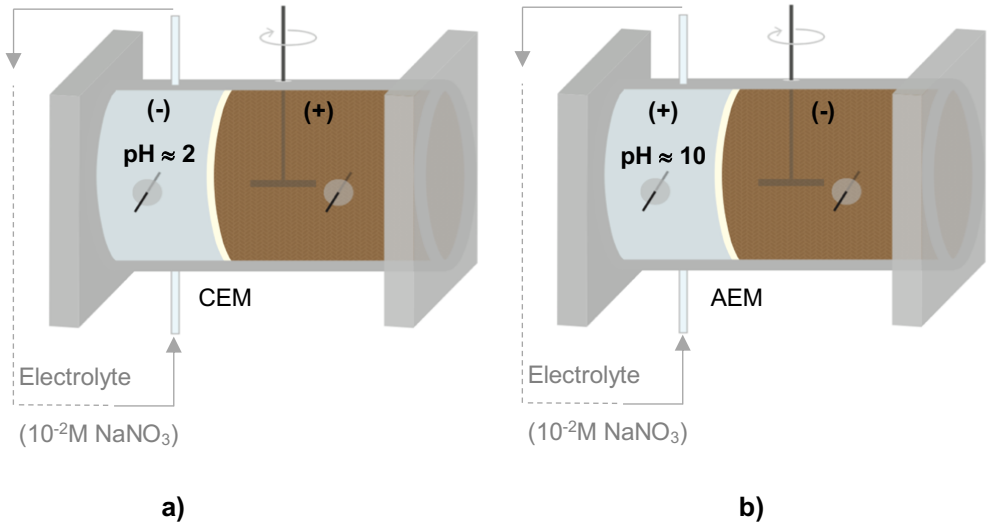


Figure 2.2 - ED set-up used with collstrop soil for As removal.

At the end of the experiments, the content of As in the different parts of the cell (membrane, electrodes, soil, water and anolyte) was analysed by a Varian 720-ES Ion Chromatography Plasma-Optical Emission Spectrometry (ICP-OES). The suspended soil was drained through filter paper to separate the solids from the liquid phase, and water content was measured too. The solid phase was dried (105

ºC), crushed by hand, digested and analysed. Membrane and electrodes were soaked in 1 M and 5 M HNO_3, respectively, for 24 h prior to analysing As in the liquid phase by ICP-OES.

Table 2.1 - Experimental conditions for the ED experiments with collstrop soil.

ED treatment (T#)	Soil CODE	Pre-treatment	Cell Type (see Figure 2.2)	Soil compartment	Liquid/Solid (mL g^{-1})	pH of electrolyte	Time (d)
T1	Original	No	a)	Anode	7	2	14
T2	Original	No	b)	Cathode	7	10	14
T2*	Original	No	b)	Cathode	7	*NA*	14
T3	Original	No	b)	Cathode	7	10	14
T4	Floc	Washing	b)	Cathode	7	10	14
T5	FF floc	Washing and sieving	b)	Cathode	7	10	14
T6	Original	No	b)	Cathode	7	10	7
T7	Original	No	b)	Cathode	7	10	3

*without pH adjustments in electrolyte
NA: not applicable

2.2.1.1. Reuse of soil in building materials - brick pellets

In order to study the suitability for further reuse in ceramics, pellets were made with treated soil from T2 in Table 2.1. Different amounts of soil were joined with pure clay (yellow wienerberger from soft-molded bricks) to test the stability of the pellets. The samples had a total weight of 2 g and 10% of distilled water was added.

Brick pellets (2 cm in diameter) were made in a form and pressed to pellets in an Instron 6022 tester at 3.14 kN. The wet pellets were weighted before being heated at a furnace with a gradual temperature increase (until 1025 ºC) where they were kept by 1 h. After cooling to room temperature, the fired pellets were weighted and characterized by porosity, density and leaching.

For porosity and density measurements, the brick pellets were placed in a desiccator under vacuum for 3 h (100 N m^{-2}). After this time, the desiccator was filled with deionized water and pellets left for 1 h. The desiccator was then opened to the air for 1 d. The pellets were weighed over and under the water ("DS/EN ISO 10545:3," 1997).

The leaching of As was also tested according to DS/EN 12457-3 (British Standards Institution, 2002). The fired pellets were crushed, and distilled water was added, L/S ratio of 2. The suspension was agitated for 16 h and the liquid phase separated from the solid particles by vacuum filtration (0.45 µm). As concentration was determined by ICP-OES.

2.2.2. Petroleum hydrocarbons removal from soil

An overview of the EK experiments carried out are shown in Figure 2.3 and the conditions are in Table 2.2. The box (inner Ø=8 cm; height=4 cm) made of Plexiglas was filled with 250 g of soil. The soil collected in Sisimiut, Greenland was initially weighted, and moisture content was determined. In order to keep the same amount of water in soil during the EKR, the soil was weight once a day in a digital balance, and water was added if needed.

Mixed metals oxide (MMO) coated titanium electrodes with a 3 mm diameter and a 5 cm length (provided by FORCE® Technology, Cathodic Protection) were used and power supply (Hewlett Packard E3612A) maintained a constant DC current. The distance between the two electrodes in EK experiments was 4.5 cm. The experiments lasted 14 d with 5 mA of current density.

The influence of the temperature was tested by comparing remediation at 22 ºC and 6º C (representative temperature of summer at Arctic). The 6º C experiments were placed inside a fridge while 22 ºC was the room temperature of the laboratory. The effect of current was assessed by comparing continuous DC with reversed electrode polarity (REP) in 24 hours intervals and also switching the current on and off every 6 hours.

The initial concentration of total hydrocarbons present in soil was performed in an external laboratory (ISQ, LABQUI; results in Appendix 2).

At the end of the EK experiments, each box was divided in two sides: anode and cathode. Total PHs (TPHs) content, elements and metals (Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S and Zn), pH, conductivity, organic content and soil morphology were analysed.

Table 2.2 - Experimental design for Sisimiut soil experiments.

Electric current strategy applied	Current intensity (mA)	Temperature (ºC)	Time (d)
Continuous	5	22	14
REP	5	22	14
On/Off	5	22	14
Control	-	22	14
Continuous	5	6	14
Control	-	6	14

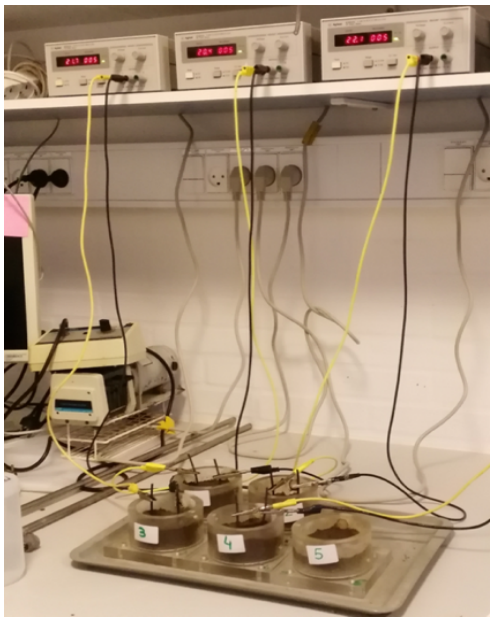


Figure 2.3 – View of the electrokinetic experiments for oil removal from polar soil.

2.2.3. EOC removal from soil

2.2.3.1. Influence of the cell design

Three different cell designs were tested (Figure 2.4. a) to c)) with three, two and one compartment. The experiments were carried out in duplicate (n=2), for 3 days (72 h) with a constant current density of 0.02 mA cm^{-2}, according to the conditions presented in Table 2.3.

Control experiments (without applied current) were also carried out for all cell designs. All the experiments were conducted in the laboratory under controlled temperature (22 ºC).

Table 2.3 - Experimental conditions for ED soil experiments.

ED experiment	Soil slurry compartment	L/S[4]	Membrane	Current density (mA cm^{-2})	Time (days)	Cell type (see Figure 2.4)
Control-3C	Central	5	AEM/CEM	-	3	a)
Control-2C	Cathode	5	AEM	-	3	b)
Control-1C	Only one	5	-	-	3	c)
3C[1]	Central	5	AEM[5]/CEM[6]	0.02	3	a)
2C[2]	Cathode	5	AEM	0.02	3	b)
1C[3]	Only one	5	-	0.02	3	c)

Legend:
[1]3C = 3 compartments cell: anode, central and cathode; [2]2C = 2 compartments cell: anode and cathode; [3]1C = 1 compartment cell, where the pair of electrodes were introduced; [4]L/S: liquid-to-solid ratio; [5]AEM: anion exchange membrane; [6]CEM: cation exchange membrane.

The experiments were carried out in cylindrical plexiglas-cells, with an internal diameter of 8 cm. The compartment where the soil was placed had a L = 10 cm and was equipped with a stirrer, whereas the electrolyte compartments had a L = 5 cm. In the 3C-cell the electrode compartments were separated from the soil compartment (central compartment) by an AEM and a CEM (Figure 2.4 a). In the 2C-cell the electrode compartment was separated from the soil compartment (cathode compartment, 2C-CAT) by an AEM (Figure 2.4 b). In the 1C-cell (Figure 2.4 c) the only compartment contained the soil slurry (electrolyte and membranes were not used).

The electrodes were platinized titanium bars, with a 3 mm diameter and a 5 cm length from Permascand®. A power supply (Agilent E3612A) was used to maintain a constant current. The ion-exchange membranes used were commercial ones from Ionics (anion exchange membrane, AEM: AR204 SZRA B02249, and cation exchange membrane, CEM: CR67 HUY N12116B). In all treatments, the soil was kept suspended in deionized water, with a L/S of 5 (75 g of soil in 375 mL of deionized water), due to continuous stirring (RW11 basic from IKA). The electrolyte was a 10^{-2} M $NaNO_3$ solution (total volume = 500 mL) without pH adjustment, being circulated at 4 mL min^{-1} in a closed system by means of a peristaltic pump (Watson-Marlow 503 U/R, Watson-Marlow Pumps Group, Falmouth, Cornwall, UK).

Conductivity and pH in the soil slurry, and the voltage between working electrodes were measured twice a day in all experiments.

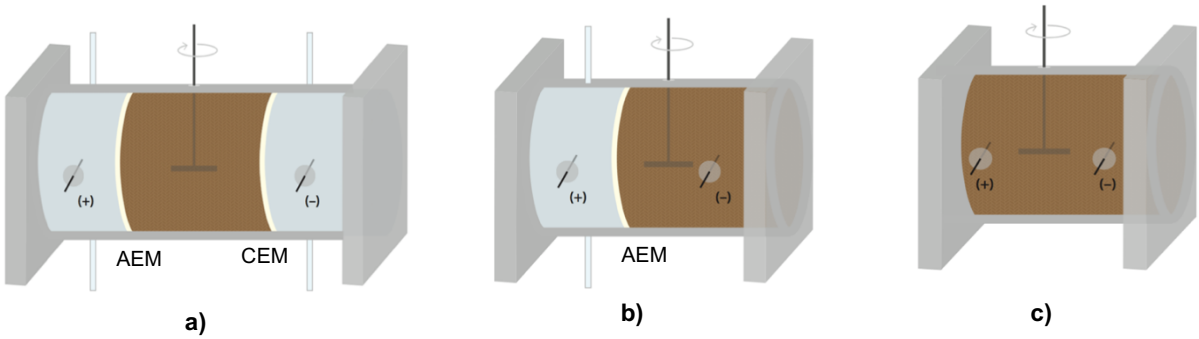
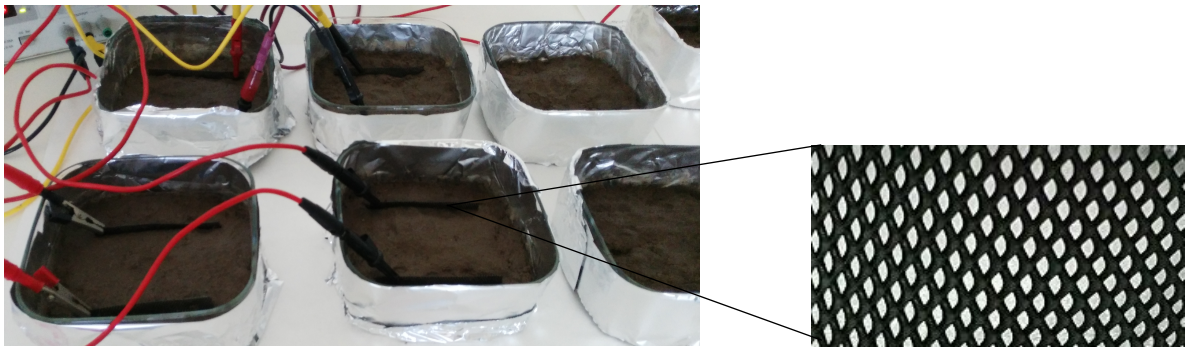


Figure 2.4 - Schematic representation of the laboratory cells used in the experiments: a) 3C-cell, b) 2C-cell, c) 1C-cell. The separation between the soil slurry and the electrode compartments was made through ion exchange membranes (AEM and/or CEM).

2.2.3.2. Electrokinetic experiments

The experiments were carried out in a simulated microcosm assembled in a parallelepiped-shaped glass container with round corners (140 x 140 x 50 mm; Figure 2.5. a) externally covered with aluminum foil (to prevent light exposure in depth). Two metal mixed oxide mesh electrodes (IrO2/RuO2-Ti; 90 x 20 x 1 mm; Figure 2.5. b)) were placed at microcosms lateral sections, 50 mm apart from each other. For each experiment, the microcosm was filled 300 g of soil and irrigated with spiked effluent (100 mL; 15 mg L^{-1} of each EOC) and left for 3 days at 6 ºC to simulate contamination aging while minimizing

biological activity. Prior beginning experiments, soil sub-samples were collected and analyzed for EOCs, moisture content, pH and conductivity.



a) **b)**

Figure 2.5 - View of a) EKR microcosms and b) metal mixed oxide coated titanium mesh electrode.

The EK experiments (made in duplicate) were carried out with a DC of 2.5 mA per 300 g of soil (power supply, Agilent E3612A) for 6 days (144 hours) at room temperature (22 ºC), without direct light exposure. Four types of current strategies were applied in the experiments (Figure 2.6.):

i) **continuous current** (CC): run with continuous DC application;
ii) **On/Off:** DC was switched off during day 3 (24 h) and turned back on at day 4;
iii) **reversed electrode polarization** (REP): electrodes polarization was reversed at day 3 for 24h;
iv) **On/Off + REP**: DC was switched off during day 3 (24 h) and turned back On with a simultaneous polarization reversion at day 4.

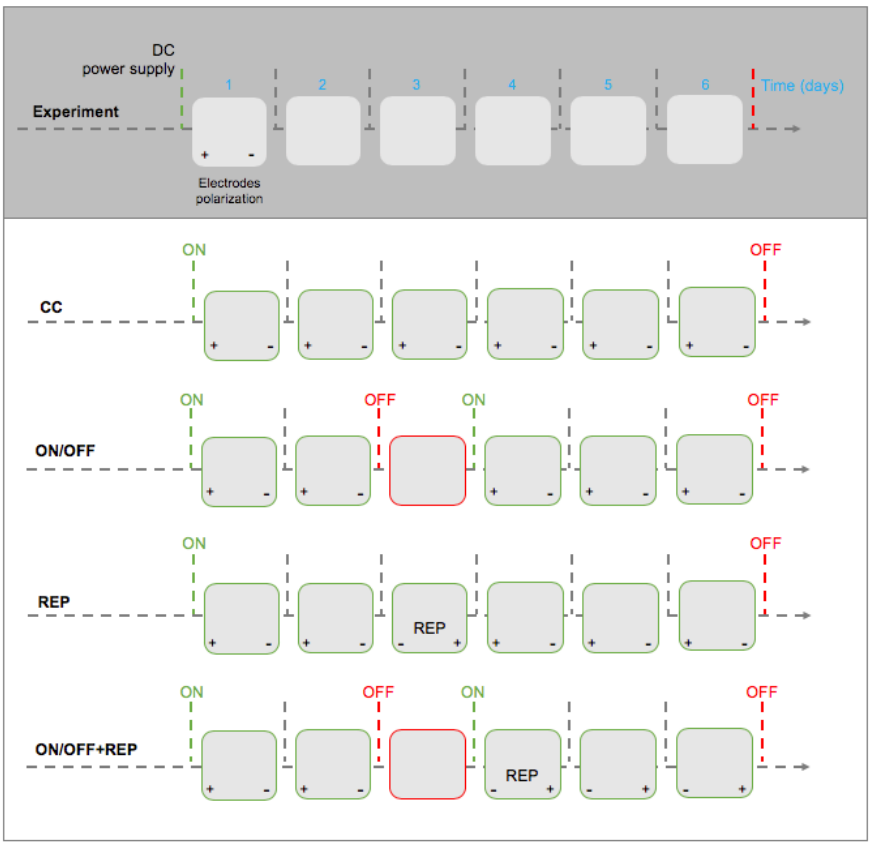


Figure 2.6 - Schematic representation of the current strategies adopted for the electrokinetic soil remediation experiments.

Along the experiment's current intensity, voltage drop between the electrodes and soil temperature were continuously monitored and microcosms were daily irrigated to keep moisture content somewhat constant (soil was weight once a day and deionized water added till initial weigh). At the end of the EKR experiments, soil layer was carefully removed and segmented into three sections: anode, central and cathode, which were immediately processed and analyzed for EOC, soil moisture, pH and conductivity.

In parallel, we performed the control experiments (duplicate) where no current was applied for the 6 days (i.e. natural attenuation control).

2.2.4. EOC removal from effluent

2.2.4.1. Simulation of constructed wetlands

To simulate constructed wetlands (CWs) two matrices were used in the experimental assays:

i) water (W) - aiming to evalute the removal efficiency in a simpler aquatic medium (deionized water) minimizing matrix interferences;
ii) wastewater (WW) - simulating more realistic conditions;

and three main variables were tested for both matrices, W and WW:

a) LECA (light expanded clay aggregate) (unplanted LECA; L);

b) *S. maritima* (only plant; P);

c) *S. maritima* and LECA (planted LECA; PL).

The experimental design of the work is in Table 2.4. and in Figure 2.7 an overview of the experiments is shown.

The experiments were carried out in glass flasks (Erlenmeyer's 500 mL) with 100 g of dried LECA and 200 mL of the liquid matrix corresponding to a L/S ratio of 2 followed by EOC spiking. Water level was maintained above the LECA surface. During the experiments the set-ups were not refilled during the assays as the loss of water was considered negligible (RSD = 6 %).

Spartina maritima with similar biomass and height were divided in groups to achieve a total plant weight of 8.0 ± 1.0 g. At the end of the assays, plants were weight and comparing to the initial value, no biomass differences were observed. The exemplars of *S. maritima* were collected in Tagus river estuary (38º36´59.39" N; 9º02´33.41" W). This species is abundant in the intertidal and have a wide geographic distribution in temperate zones. This species belongs to lower zone of a salt marsh having characteristics to a partial or total submergence, high soil salinity and soil anoxia (Mateos-Naranjo et al., 2010). After collection, plants were immediately transported to the laboratory in controlled conditions (refrigerated and avoiding light exposure). The roots were thoroughly washed to remove any sediment particles attached to their surface, submersed (approx. 1 min) in a solution with sodium hypochlorite (0.5%) to stop microbial action and rinsed with deionized water (approx. 30 s). Experiments were then started. Plants were analyzed according to the procedure of Lichtenthaler and Wellburn (Lichtenthaler, H.K., Wellburn, 1983). Briefly, leaves were cut in small pieces (0.20 ± 0.06 g) and put in glass tubes in a solution of 80% of ACE (10 mL) in darkness. Tubes were manually agitated twice per day. After 48 h, the target wavelengths were read on a spectrophotometer (UV-Visible Thermo Spectronic Helios Gamma).

The W1 and W2 were carried out in May. The WW1 was carried out in June and the WW2 in October. The applied treatments were compared in each assay but not between assays (W and WW).

Table 2.4 - Experimental design of the simulated CWs experiments.

Assay	#	CODE	Variables	Time (d)	EOC (mg)	Presence of light
W	1	W1-L	LECA	3	0.2	No
	2	W2-L	LECA	7	0.2	No
		W2-P	Plant			
		W2-PL	Plant and LECA			
WW	1	WW1-L	LECA	7	0.2 – 0.8 [a]	Yes
		WW1-P	Plant			
		WW1-PL	Plant and LECA			
	2	WW2-L	LECA	7 plus 7	0.1 – 0.3 [b]	No
		WW2-P	Plant			

Legend:
[a] Flasks were spiked at days 0, 2, 4 and with 0.2 mg for each time making the mass range from 0.2 to 0.8 mg.
[b] Flasks were spiked at days 0, 3, 6 and 7, 10, 13 making the mass range from 0.1 to 0.3 mg for each cycle.
Controls were also carried out with spiked matrices without LECA and *S. maritima* (W#-C and WW#-C).

Figure 2.7 - Overview of the experimental set-up for the simulated CWs at laboratorial scale.

Water assays (W) were operated in a batch mode, i.e. only one EOC spiking dose at time 0. Wastewater assays (WW) were carried out in fed-batches mode, i.e. EOC spiking in pulses at specific times. Both systems were carried out under laboratory conditions at room temperature (22 ± 2 ºC) and in duplicate (n=2).

- W assays were divided in:
  - W1: 3 days to assess L removal efficiency in short periods of time;
  - W2: 7 days to assess L, P and PL removal efficiency in the hydraulic retention time used for both mesocosms studies and full scale CWs (Weber and Legge, 2011).

Both assays (W1 and W2) were spiked with 0.2 mg of each contaminant and carried out under dark conditions.

- WW assays were divided in:
  - WW1: 7 days to assess L, P and PL removal efficiency simulating successive arriving of contaminants (i.e. controlled experimental microcosm spiked every two days (0, 2, 4 and 6 days) making the mass of each contaminant range between 0.2 and 0.8 mg). The higher mass of contaminants aimed to assess the mobilization and/or contaminants removal testing harsh field conditions. This assay was carried out under sunlight exposure (EOC photodegradation as a possible contributor for remediation);
  - WW2: 7 days to assess L, P and PL removal efficiency simulating successive arriving of contaminants (i.e. controlled experimental microcosm spiked every three days (0, 3 and 6) making the mass range between 0.1 and 0.3 mg) followed by effluent drainage and re-fill with fresh effluent for a second 7-days cycle following the same spiking scheme. Contaminants' concentration were decreased to values more similar to those reported in WWTPs (Heberer, 2002b). This assay was carried out in dark conditions at the substrate level to simulate real light field conditions. From the 3 contaminants previously tested, only the two with lower removal efficiency observed in WW1 (CAF and MBPh) were used aiming to improve system removal efficiency.

- Controls were also carried out to test:
  - the self capacity of the system to decrease EOC levels – only spiked matrix (deionized water and wastewater, W#-C and WW#-C, respectively);
  - plants vitality (CV) in the sytems – plants in non-spiked matrix with LECA (CV_{LECA}) and without LECA ($CV_{w/o\ LECA}$).

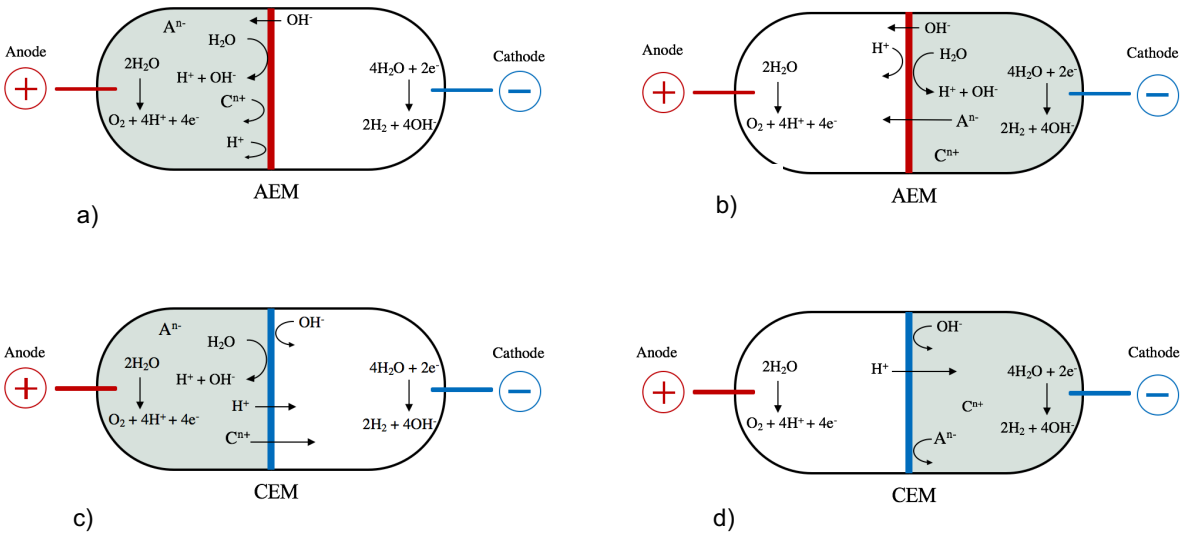
2.2.4.2. Electrodialytic experiments

The 2C ED-cell design was tested for EOC removal from effluent in accordance to the designs presented in Figure 2.8. a) to d). The cell was assembled with two compartments (cathode and anode both with an internal diameter of 8 cm) separated by an ion exchange membrane (either an anion exchange membrane, AEM: AR204 SZRA B02249 or cation exchange membrane, CEM: CR67 HUY N12116B, both from Ionics Inc., Massachusetts, USA). The electrodes were platinized titanium bars (diameter 3 mm) obtained from Permascand® and a power supply (Hewlett Packard E3612A) was used to maintain a constant current. Electrodes were installed 5 cm apart from each other.

One of the compartments was filled with effluent and the other with electrolyte. The fresh electrolyte was a 10^{-2} M $NaNO_3$ solution with pH 6.4±0.4 and conductivity of 1215±62 μS cm^{-1}. The electrolyte (total volume = 500 mL) was recirculated by means of a peristaltic pump at 4 mL min^{-1} (Watson-Marlow503 U/ R, Watson-Marlow Pumps Group, Falmouth, Cornwall, UK) in a closed circulation system. The effluent was spiked with a mixture of 3 mg L^{-1} of each compound (CAF, BPA, E2, EE2 and MBPH) in 1:1 MeOH:Acetone. The effluent (300 mL) was placed either in the anode or cathode compartment, and either a cation or anion exchange membrane were used for separating the compartments. The experiments were carried out for 12 h with current intensity applied of 20 mA.

To assess EOC removal kinetics, samples were collected hourly (total of 12 h). The control experiments without applied current were also carried out (one with anion, Control.AEM, and another with cation exchange membrane, Control.CEM, separating the compartments). The experimental design is shown in Table 2.5.

All the experiments were carried out in dark conditions and at controlled room temperature (22 °C).



Legend:
AEM: anion exchange membrane; CEM: cation exchange membrane.
Electrodialytic (ED) experiments:
A.AEM and A.CEM: effluent placed in anode compartment using AEM and CEM, respectively.
C.AEM and C.CEM: effluent placed in cathode compartment using AEM and CEM, respectively.

Figure 2.8 - Schematic representation of ED cell set-ups (a) A.AEM; (b) C.AEM; (c) A.CEM; (d) C.CEM.

Table 2.5 - Experimental design for the ED with effluent and EOC.

	Experiment CODE	Effluent sample Code (Eff#)	Effluent compartment	Membrane	Figure	Time (h)	Current (mA)
Controls	Control.AEM	Eff1	*	AEM	-	12	0
	Control.CEM	Eff1	*	CEM	-		
ED experiments	A.AEM	Eff2	Anode	AEM	a)	12	20
	A.CEM	Eff2	Anode	CEM	c)		
	C.AEM	Eff2	Cathode	AEM	b)		
	C.CEM	Eff2	Cathode	CEM	d)		

Conductivity, pH and the voltage drop between working electrodes were measured during the experiments. For phosphorus analysis, electrolyte and effluent samples were collected at the beginning and at the end of each experiment and analyzed in accordance to Section 2.5 procedure.

2.2.4.3. Electrokinetic experiments

Electrochemical experiments were carried out in a reactor cylindrical-shaped made of Plexiglas with a length of 10 cm and internal diameter of 8 cm. Electrodes were installed 2.5 cm from the middle of the reactor (5 cm apart from each other). The power supply (Hewlett Packard E3612A) was used to maintain a constant DC. The experimental conditions are in Table 2.6. The effluent was spiked with 2 mg L^{-1} of each EOC.

- *Vertical EK reactor working in continuous flow mode*

The vertical cell was tested in a continuous flow mode with effluent at 2 mL min^{-1} (Figure 2.9. a)). The Pt/Ti electrode was fixed as cathode and Pt/Ti and graphite (99.9995% metals basis; length 80 mm, diameter 3 mm; AlfaAesar) were tested as anodes, with two different current intensities: 25 mA and with 4 times more of current intensity (100 mA). The effluent was spiked with 3 mg L^{-1} of SFM, CBMP, BPA, EE2, DCF and MBPh;

- *Horizontal EK reactor working in batch mode*

A EK reactor with both electrodes in contact with effluent is in Figure 2.9. b). The experiments in batch mode were tested and optimized in terms of anode working material with a fixed cathode (activated titanium bar coated with mixed metal oxides (MMO), IrO_2 and RuO_2). The characteristics of the electrodes used are presented in Table 2.7. After selecting the best anode, different current intensities (100 mA, 125 and 175 mA) were tested in order to find the best EK conditions for the final set-up. The effect of cathode in EOC was studied replacing for the same anode material and shape. Here the effluent samples were taken every 30 minutes to study EOC removal kinetics. Using the electrode material that showed higher EOC removals and less energy consumption (higher efficient

conditions), a scaling up of two-fold was done for proof-of-concept. A electrochemical reactor of 20 cm long (internal diameter of 8 cm) and 900 mL of effluent were used. To account the doubled size (900 mL of effluent), a sequence of four electrodes (anode-cathode) were used interchangeably (Figure 2.9. c)). The proof-of-concept (n=2) was carried out at 175 mA (splited in the four electrodes) of current density for 2 hours;

- *Integrated EK/ED treatment with 1C and 2C-cells*

The combination of 1 and 2C was performed with best working parameters previously found in the experiments: working anode, cathode, current intensity and membrane (Figure 2.9. d)). The experiments performed.

All the experiments were carried out in dark conditions and controlled room temperature (22 °C). Conductivity, pH and the voltage drop between working electrodes were measured in the beginning and at the end of the experiments.

The effluent characteristics used for the experiments are in Appendix 3, as well as, a more detailed overview of the experimental design in Appendix 4.

Table 2.6 - General experimental set-ups tested for EOC from effluent by EK process.

Cell design	Mode	Time (h)	Current intensity (mA)	Cathode material;shape	Anode material;shape	Effluent compartment
1C	Vertical flow	2 mL min^{-1}	25 100	Pt/Ti;bar	Graphite;bar Pt/Ti;bar	-
1 C	Batch (horizontal)	2	100	MMO;bar	Pt/Ti;bar Pt/Ti;mesh MMO;bar MMO;mesh MMO;circular mesh	-
1 C	Batch (horizontal)	2	125 175	MMO;bar	MMO;circular mesh	-
Proof-of-concept	Batch (horizontal)	2	175*	MMO;circular mesh	MMO;circular mesh	-
1 C + 2 C	Batch (horizontal)	4 (2h + 2h)	175	MMO;circular mesh	MMO;circular mesh	1C + cathode
2 C + 1 C	Batch (horizontal)	4 (2h + 2h)	175	MMO;circular mesh	MMO;circular mesh	anode + 1C
1C + 2C + 1C	Batch (horizontal)	8 (2h + 4h + 2h)	175	MMO;circular mesh	MMO;circular mesh	1C + cathode

*split in two: 87.5 mA

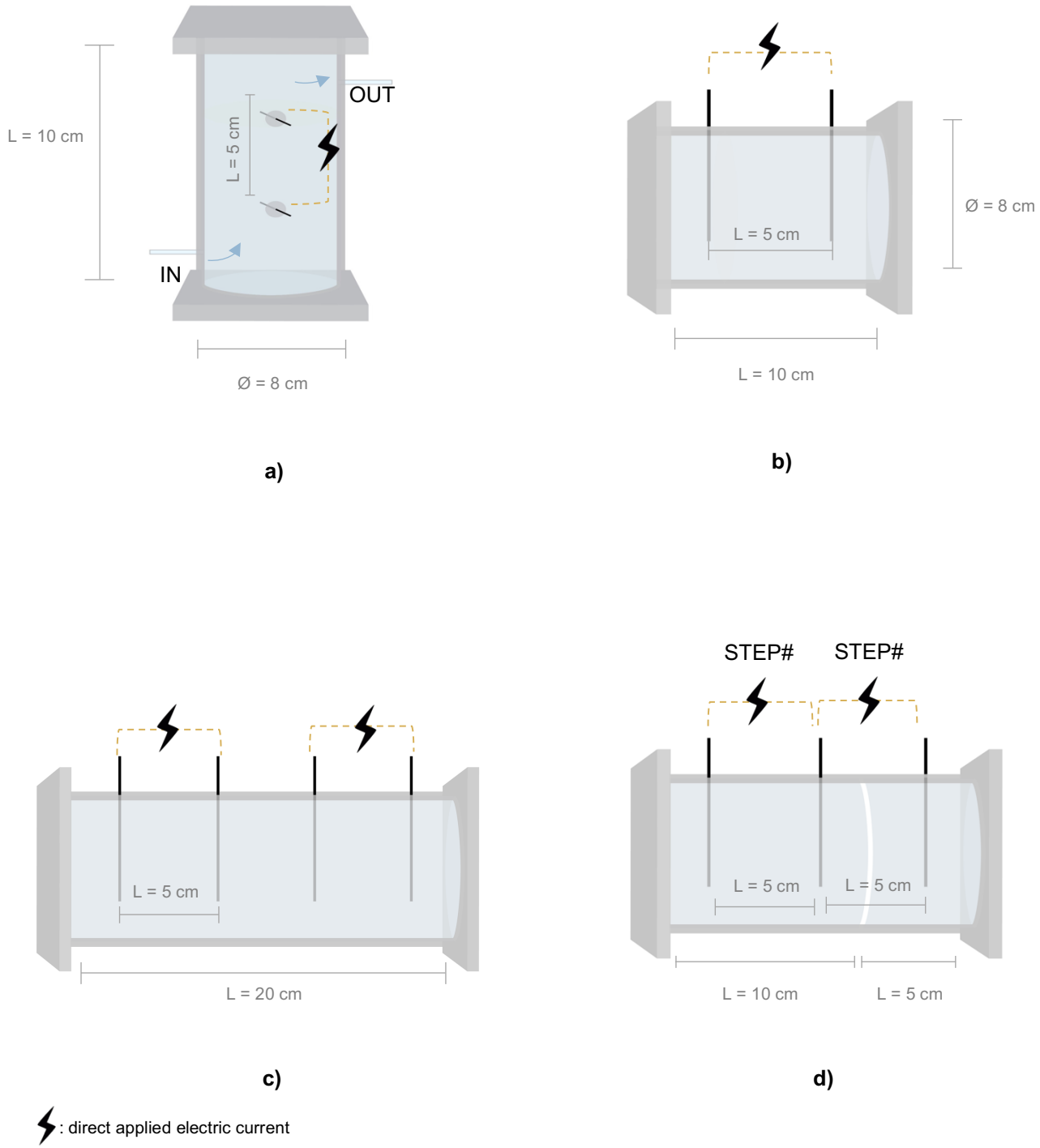
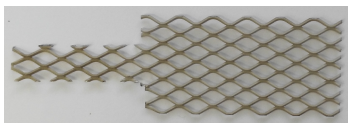
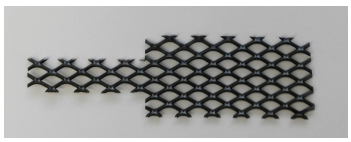
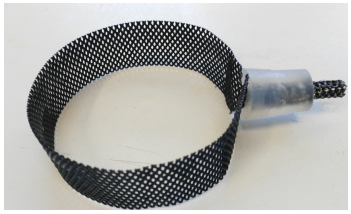


Figure 2.9 - Schematic representation of the laboratory electro-chemical reactors used in the experiments with effluent: a) EK vertical continuous flow reactor; b) horizontal EK reactor working in batch mode; c) proof-of-concept of reactor c); d) combination between 1C and 2C-cell using anion exchange membranes (AEM) to separate the compartments.

Table 2.7 - Electrode material specifications used in EK experiments with a single reactor working in batch mode for effluent treatment.

Material	Shape	Dimensions	Submerged area* (cm^2)	Electrodes picture	Supplier
Pt/Ti	Bar	Ø = 3 mm L = 5.5 cm	5.32		Permascand®
MMO (IrO_2+RuO_2) coated titanium	Bar	Ø = 3 mm L = 5.5 cm	5.32		Force®
DSA Pt/Ti	Mesh	L = 6.0 cm W = 3.2 cm T = 0.2 cm	33.90		Inagasa®
DSA MMO (IrO_2+RuO_2) coated titanium	Mesh	L = 5.4 cm W = 2.9 cm T = 0.15 cm	22.50		Inagasa®
DSA MMO ($IrO2$+RuO_2) coated titanium	Circular mesh	Ø = 6.0 cm W = 2 cm T = 0.1 cm	105.80		Force®

Legend:
L = Length; W = Width; Ø = Diameter; T = thickness
DSA: Dimensionally Stable Anode; MMO: Metal Mixed Oxide (Ir, Ru); Pt/Ti = Platinized titanium
* area that was in contact with the effluent while the experiment

2.3. Analytical methodologies

2.3.1. Chemicals and solvents

Acetonitrile (ACN), methanol (MeOH), acetone, formic and acetic acid were HPLC grade purchased from Sigma–Aldrich. Sodium nitrate ($NaNO_3$) was reagent grade from Panreac and sodium hydroxide (NaOH) from Sigma-Aldrich. All the other used solvents were from Merck (Darmstadt, Germany) and Sigma–Aldrich (Steinheim, Germany). Deionized water was purified with a Milli-Q plus system from Millipore (Bedford, MA, USA). Caffeine, sulfamethoxazole, carbamazepine, bisphenol A, 17β-oestradiol, ethinylestradiol, ibruprofen, diclofenac and oxybenzone standards were purchased from Sigma-Aldrich (Steinheim, Germany) with high purity grade (>97%).

2.3.2. General parameters for soil samples

pH: dried soil (5.0 g) was agitated with 12.5 mL of deionized water or KCl for an hour and pH were measured after letting the sample stand for 10 min (until the liquid is separated from the soil) using a radiometric analytical electrode.

Conductivity: dried soil (10.0 g) was agitated with 25 mL of distilled water for 30 min and conductivity was measured after letting the sample stand for 10 min (until the liquid is separated from the soil) using a radiometric analytical electrode.

Organic content: the content of organic matter was found as a loss on ignition after 1 h at 550 ºC.

Water content: water content was calculated as weight loss at 105 °C for 24 h.

Carbonate content: carbonate content was determined volumetrically by the Scheibler method (2.5 g of soil reacting with 20 mL of 10% HCl). The amount was calculated, and all the present carbonate was assumed as calcium carbonate.

2.3.3. Collstrop soil

2.3.3.1. Soil characteristics

The soils were characterized by the following parameters: As concentration, pH, conductivity, organic matter, carbonates contents and grain size distribution. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) analysis was also carried out. The grain size distribution was obtained by means of laser diffraction method performed with Mastersizer 2000 (Malvern Instruments). The measurements were conducted in a liquid dispersion with a peptising agent.

2.3.3.2. Arsenic extraction and analysis

The solid suspension was filtrated by vacuum and the As concentration was measured after digestion following the method describes in Danish Standard (DS) 259 (Danish Standard DS 259, 2003): 20.0 mL of 10 M HNO_3 was added in 1.00 g of dry soil and heated at 200 kPa (120 ºC) for 30 minutes.

The liquid obtained from the filtration was thereafter separated by vacuum filtration through a 0.45 µm filter and diluted to 100 mL with deionized water.

The As concentration was analysed by ICP-OES. A blank was analysed between samples to guarantee the quality of the results. In addition, quality control standard solutions were run periodically between the samples.

Mass balances, defined as the relation between the sum of mass found in the different ED cell compartments at the end of the experiments and the amount initially found in the mass of untreated soil placed in the ED cell, were made for control purposes.

2.3.3.3. pH desorption tests

The effect of pH on As desorption was assessed by suspending 2.5 g dry original soil in 25 mL HNO_3 or 25 mL NaOH with concentrations ranging between 0.01 M and 1.0 M. After filtration (0.45 µm), the As concentrations were measured in the liquid phase by ICP-OES. Extractions in distilled water were made as reference. Extractions were made in duplicate.

2.3.3.4. Sequential extraction

Sequential extraction was performed based on the improvement of the three-step method (also known as BCR), with an extra residual step. The method is described in Standards, Measurements and Testing Program of the European Union (Pueyo M Mateu J Rigol A Vidal M López-Sánchez J Rauret G, 2008). The dried soil was crushed and 0.5 g was treated in four steps as follows: (1) exchangeable and acid soluble: extraction with 20.0 mL of 0.11 M acetic acid (CH_3COOH) (pH 3) for 16 h, (2) reducible: extraction with 20.0 mL of 0.1 M of hydroxyammonium chloride ($NH_2OH{\cdot}HCl$) (pH 2) for 16 h, (3) oxidizable: change from reducing to oxidizing condition, performed by extraction with 5.0 mL of 8.8 M of hydrogen peroxide (H_2O_2) for 1h and heating to 85 ºC for 1 h with a lid followed by evaporation of the liquid at 85 ºC until it had been reduced to less than 1 mL by removal of the lid. The addition of 5.0 mL of 8.8 M H_2O_2 was repeated, followed by resumed heating to 85 ºC for 1 h and removal of the lid for evaporation until almost dry. After cooling, 25.0 mL of 1 M $(NH_4)OOCCH_3$ (pH 2) was added, and extraction lasted for 16h, and (4) residual fractions: digestion according to DS 259 (described above). Between each step (excluding the residual fraction) the sample was centrifuged at 3000 rpm for 15 min, and the supernatant was decanted and stored for Varian 720-ES ICP-OES analysis. Before the addition of each new reagent, the sample was washed for 15 min with 10.0 mL of distilled water and centrifuged at 3000 rpm for 15 min, and the supernatant was then decanted and discharged. All extractions were performed at room temperature, and samples in each step were made in duplicate.

2.3.4. Polar soil

2.3.4.1. Soil characteristics

The main properties of the studied soil were analysed: water content, organic matter, pH, conductivity and carbonate content. The procedures can be found in *Section 2.3.2. General parameters for soil samples*. Laser and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) analysis was also carried out.

2.3.4.2. Petroleum hydrocarbons extraction and analysis

The soil samples were prepared with an internal standard consisted of three stock solutions with monobrobenzene, o-terphenyl and squalan in pentane. The concentration was 10 g L^{-1}. 1000 µL of each stock solution was added to a 100 mL volumetric flask which was filled with pentane. Hereby the concentrations of the internal standards were 100 mg L^{-1}.

For oil extraction, 60 g of soil was shaken together with 20 mL pentane in a 100 mL redcap glass, the shaking stopped after reaching a liquid suspension (after about 30 s of handshaking). 20 mL pentane

with internal standard was added to the sample and it was placed at a shaking table at 150 rpm for 24 h. The organic phase was taken into the vial from where further analyses were carried out. The oil content of the polluted soil was determined by Gas Chromatography using a Flame Ionization Detector (GC-FID, 6890N). The column used was an Agilent® J&W GC columns DB-1HT (30 m, 0.25 mm, 0.10 µm). The oven temperature ranged from 50 ºC to 350 ºC at 10 °C/min (hold 3 and 7 min). The detector was set to a temperature of 315 ºC, and the used thermal ramps were as follows: initial temperature of 50 ºC for 3 min followed by a gradient of 10 ºC min until a temperature of 250 ºC to be maintained for 7 min, and then, another gradient of 10 ºC min until a final temperature of 350 ºC. The used carrier gas was high purity air, hydrogen with a flow of 40 mL min^{-1}. Finally, the injection of the samples was automatic (1 µL) in splitless (1 min) mode. Pentane controls and blinds were also run randomly in the line sequence.

Quantification of initial TPHs in the range of C10 to C40 was measured externally at a licensed laboratory following ISO/DIS 16703 (LABQUI - *Lab. Química e Ambiente*).

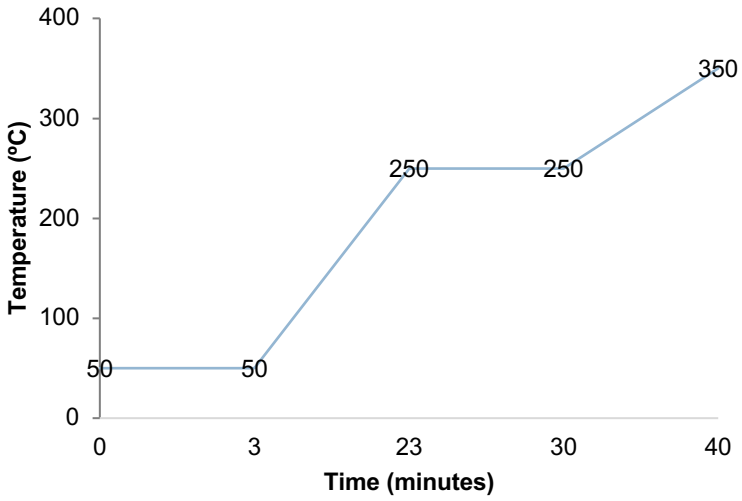


Figure 2.10 - Oven temperature for PHs analysis in GC.

2.3.4.3. Metals and other elements extraction and analysis

The metals and major elements were measured after digestion: 20.0 mL (1:1) HNO_3 added in 1.0 g of dry soil were autoclaved (200 kPa, 120 ºC for 30 minutes). Solid particles were subsequently removed by vacuum filtration through a 0.45 µm filter and the liquid was diluted to 100 mL. The concentrations in the filtrate samples were analysed by ICP-OES (Varian 720-ES). The digestion method is described in Danish Standard (DS) 259 (Danish standard, 2003).

2.3.5. Agricultural soil

2.3.5.1. Soil characteristics

Physico-chemical characterization of the soil was performed by the Research Unit of Environmental and Natural Resources (*Unidade de Investigação Ambiente e Recursos Naturais*, UIARN) at the National Institute for Agricultural Research located in Oeiras, Portugal.

2.3.5.2. EOC extraction from soil slurry

By the end of the experiments, the soil slurry was filtered under vacuum and separated in liquid (water) and solid phase (soil). The liquid phase was filtered through MFV-5 glass microfiber filters (diameter 47 mm, pore size 0.7 μm) from Filter-Lab (Barcelona, Spain) and then extracted by SPE (Section *2.3.6.2. EOC extraction from effluent/liquid samples*).

The soil was extracted (n=3) following a QuEChERS (quick-easy-cheap-effective-rugged-safe) adapted from (Bragança et al., 2012). Extract tubes were obtained from Waters (Dublin, Ireland). The acetate buffer contained 1.5 g NaOAc and 6 g $MgSO_4$. The dispersive phase contained 150 mg PSA (primary and secondary amine) and 900 mg $MgSO_4$. A 5 g of homogenized soil was weighed in a 50 mL polypropylene centrifuge tube with 3 mL of purified water (pH of 2.50 adjusted with HCl) and manually shaken. Then, NaOAc and $MgSO_4$ was added and swirled on a vortex mixer for 4 min with higher speed, following 4 min in an ultrasonic bath. After that, 7 mL of acetonitrile (1% HCOOH) was added, agitated in a vortex (4 min) and placed in an ultrasonic bath for 4 min. Then, the extract was centrifuged at 4000 rpm for 10 min. An aliquot of the supernatant (acetonitrile phase) was transferred to a 15 mL centrifuge tube containing the PSA and $MgSO_4$, and was manually shaken for 10 s and swirled on a vortex mixer for 60 s. After this step, the extract was centrifuged again (4000 rpm for 10 min), and 4 mL supernatant were transferred to a glass vial. The extract was evaporated under a gentle stream of nitrogen till 0.5-1 mL.

2.3.5.3. EOC extraction from soil

The soil was extracted (n = 2) following a QuEChERS method adapted from (Pinto et al., 2010). Extract tubes were obtained from Waters (Dublin, Ireland). A 2.5 g of homogenized soil was collected immediately and weighted in an analytical balance; 1.5 mL of deionized water was added afterwards and mixed in a vortex (approx. 15 s); 2.5 mL of acetonitrile was added and swirled in the vortex for 1 min; 1 g MgSO4 was added, and vigorously shaken (manually) for 6 s followed by vortex for 30 s. Samples were then centrifuged at 5,000 rpm for 5 min. The supernatant (organic aliquot phase) was collected and filtrated through PTFE syringes filters (previously passed through acetonitrile). All samples were stored at 6 ºC until analysis.

2.3.6. Effluent

2.3.6.1. Effluent characterization

The initial effluent characterization was performed by the WWTP laboratory.

2.3.6.2. EOC extraction from effluent/liquid samples

The effluent samples were pre-cleaned/concentrated by solid phase extraction (SPE) using Oasis HLB 500 mg (Waters; Saint-Quentin En Yvelines Cedex, France). The cartridges were placed in an SPE manifold connected to a vacuum pump and operated as follows: conditioned by washing with 3 × 6 mL of MeOH, followed by re-equilibrium with 3 x 6 mL of Milli-Q water; for EOCs enrichment, samples were acidified to pH 2 before extraction (nitric acid; deionized water, 1:1) , and filtered through 0.45 μm MF filter; 200 mL of sample was passed through the cartridge at a flow-rate of approx. 10 mL min^{-1}; then cartridges were dried for *ca*. 2 min by vacuum; finally extracts were eluted with 2 × 6 mL of MeOH. Whenever needed, extracts were concentrated under a gentle stream of nitrogen. Extracts were kept at 5 ºC until analysis. Before analysis, each sample was filtered through FILTER-LAB® polytetrafluoroethylene (PTFE) syringes filters (pore size of 0.45 μm), previously passed through methanol. The EOC recoveries for T0h and T2h (time of the EK experiments) are in Appendix 6 and 7. The recoveries ranged from 68±2% and 102±10%, corresponding to BPA and EE2. Recoveries were between 80% and 120% for the spiked electrolyte and deionized water samples (results not shown).

2.3.7. EOC analysis

The general procedure for the EOC analysis after EK/ED experiments is in Figure 2.11.

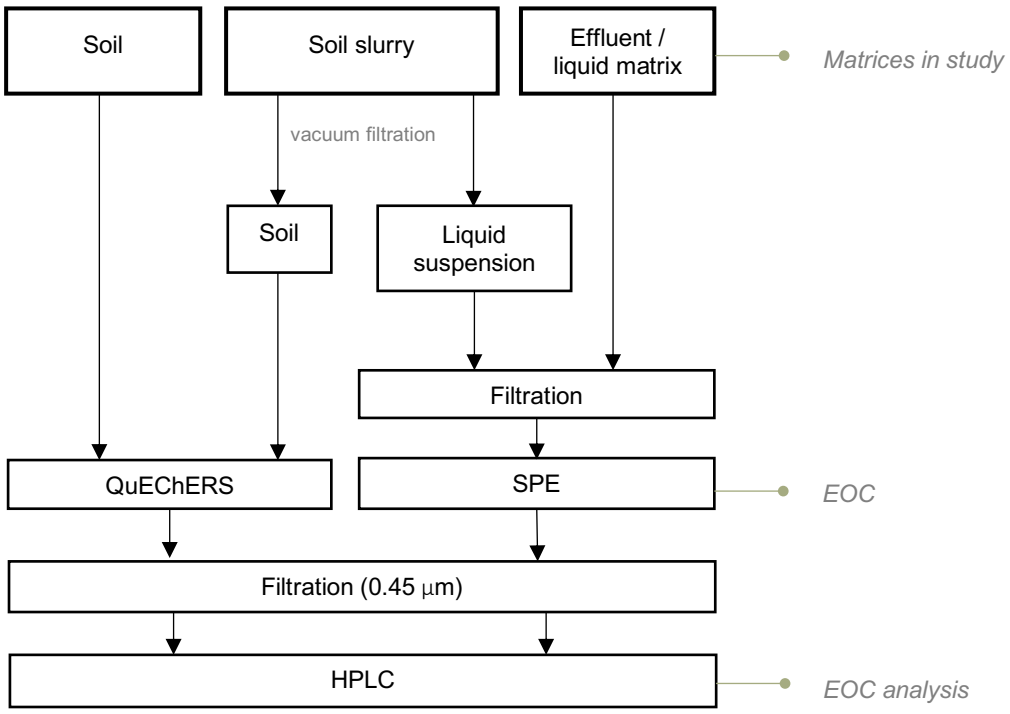


Figure 2.11 - General procedure for soil, soil slurry, and effluent used after experiments for EOC analysis.

The EOC analysis were carried out by high-performance liquid chromatography (HPLC) with a diode array and fluorescence detectors (HPLC–DAD-FLD), 1260 Infinity II LC Systems (Agilent 1100 Series Technologies, USA) equipped with a quaternary pump and auto-sampler (1260). The RP-18e column (Chromolith High Resolution, 100 × 4.6 mm; VWR, Darmstadt, Germany) was used for analytes separation. For data process the LC OpenLab software was used.

HPLC analysis was performed on equipped with 1260 Infinity II Quaternary Pump (G7111B) with an operating pressure of up to 600 bar and up to 10 mL min^{-1}, a 1260 vial sampler (G7129A), and a diode array detector (G1315B) from Agilent 1100 Series. The fluorescence detector (G1321A) was also from Agilent, and the UV wavelength was set to scan from 220 nm to 400 nm.

For the works in Section *2.2.4.1. Simulation of constructed wetlands* and *2.2.3.1. Influence of the cell design,* the EOC analysis were performed in HPLC, Finnigan MAT HPLC system from Thermo Scientific, USA equipped with a SP P4000 Pump, an AS 3000 autosampler, a diode array detector (DAD; TSP Spectra SYSTEM UV6000LP) and a TSP SN 4000 interface. The wavelength was set between 200 nm and 800 nm. The analytes separation was carried out using Chromolith HighResolution RP-18e column with 100 × 4.6 mm from VWR (Darmstadt, Germany) and Onyx SecurityGuard C18 cartridges (5 × 4.6 mm) from Phenomenex (Torrance, USA).

All HPLC runs were performed at a constant flow of 1 mL min^{-1}, in gradient mode, with the oven set to 36 ºC. A mixture of ACN/Mili-Q water/formic acid was used as eluent (A: 5/94.5/0.5 % and B: 94.5/5/0.5 %) with a gradient of 97% of A (0-15 min) followed by 95% of B, until 50 min, and 97% of A, until 55 min.

An initial chromatogram of the nine EOC in study is in Appendix 8, and the LD and LQ of the method in Appendix 5.

2.5. Statistical analysis

Statistical analysis was carried out using the GraphPad software, one-Way ANOVA Tuckey pairwise comparisons test, at 95% confidence level (p<0.05) when applicable.

SECTION III

3. RESULTS AND DISCUSSION

3.1. As removal from soil

3.1.1. Collstrop soil characteristics

The characteristics of the original soil are summarized in Table 3.1. The soil has a sandy loam texture (6% clay, 43% silt and 51% sand) according with USDA soil classification system, with slightly acid pH and with a low carbonate content, which means a low buffer capacity.

The site where the soil was collected showed to be heavily contaminated with As with an initial concentration of 594 mg As kg^{-1} of soil, which means that As contamination exceed the soil quality criteria in Denmark (20 mg kg^{-1}) by 30 times (Miljøstyrelsen (Danish EPA), 2015).

Table 3.1 - Initial characteristics of Collstrop soil.

Type of soil	As (mg kg^{-1})	pH_{KCl}	pH_{H2O}	Conductivity (mS cm^{-1})	Carbonate content (%)	Organic matter (%)	Grain size distribution (%)		
							Clay	Silt	Sand
Sandy Loam	594 ± 100	5.4 ± 0.05	6.3 ± 0.3	0.2 ± 10	2.2 ± 0.04	19 ± 1	6	43	51

3.1.2. 2C-cell with electrolyte pH adjustmens

3.1.2.1. General results

The voltage and conductivity (Figure 3.1) were similar between the two tretments. From the beginning of the treatment until the end, the voltage gradually dropped followed by a stabilization tendency. This pattern is observerd due to the production of ions from electrolysis at the electrodes (H^+ or OH^-) and also other ions released from soil, which increase the conductivity and decrease the resistance of the ED process. Without pH adjustments in electrolyte (Treatment T2*) the soil slurry conductivity slightly increased (0.3 to 0.5 mS cm^{-1}) and the voltage slowly decreased over the time from 10.9 to 7.5 V (results not shown).

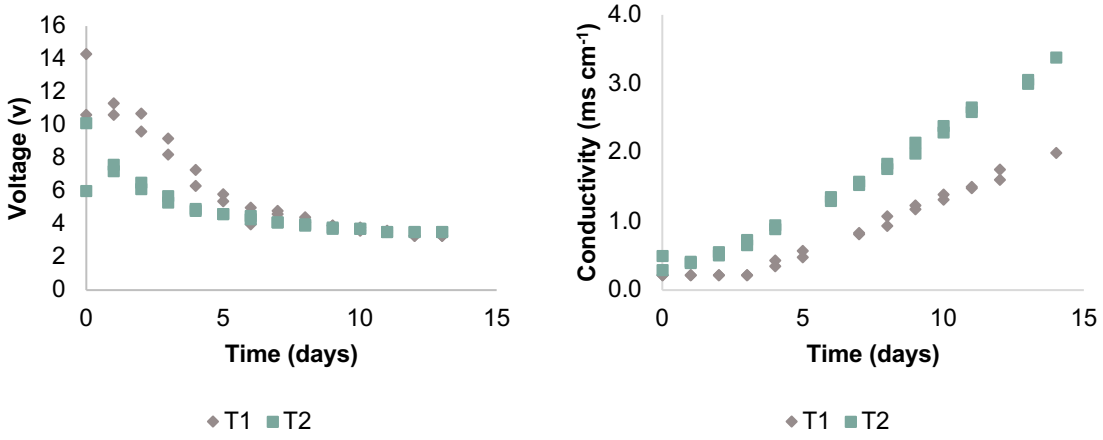


Figure 3.1 - Voltage and conductivity over the cells during the ED treatment for T1 and T2.

Due to water electrolysis the pH of the soil slurry changed according with the compartment (Figure 3.3): when the soil slurry was placed in the anode (T1) the pH decreased until ≈2 whereas when placed in the cathode (T2 and also T2*) the pH increased abruptly until 10 after 24h of applied current and to 11, remaining constant until the end of the experiment.

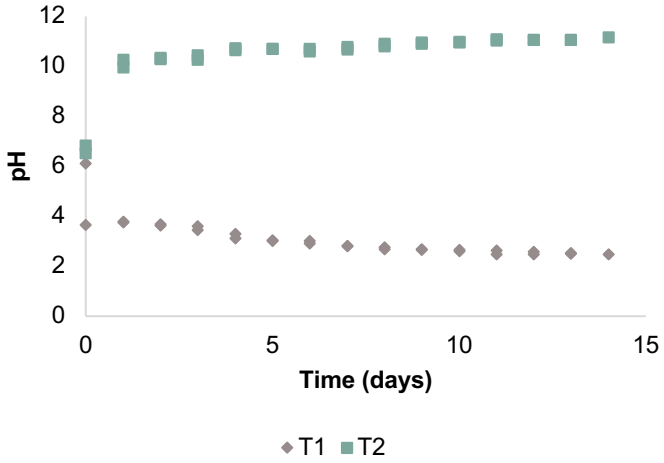


Figure 3.2 - pH variation in the soil slurry during ED treatment.

3.1.2.2. As removal

An overview of As removal after ED treatment when the soil was placed either in anode (T1) or cathode (T2) with pH adjustments in the electrolyte is in Table 3.2. This work showed that the electrode compartment where the contaminated soil is located is crucial for As removal due to the prevailing pH changes.

The mass balances of As, defined as the recovered amount of an element in percentage of the initial amount, ranged between 77-99%. Imperfect mass balances are expected considering inhomogeneous distribution of the As in the industrially polluted soil (Jensen et al., 2007). In the present work, the values indicate an acceptable quality of the experiments and the validity of the results presented.

The As removal in percentage was calculated as mass of all As at the end of the experiment (water + electrolyte + membrane + electrode) minus the As concentration in the soil divided by the total mass found in all parts of the cell (soil + water + electrolyte + membrane + electrode) at the end of the experiment. The removal efficiency of As by ED ranged between 3% and 80% corresponding to the amount of 31 mg As kg^{-1} and 475 mg As kg^{-1}.

Overall the distribution pattern of As in the different ED cell compartments differed significantly when compared with acid and alkaline pH cell-conditions and results are in Figure 3.3.

Table 3.2 - Overall results of ED treatments in As removal from soil.

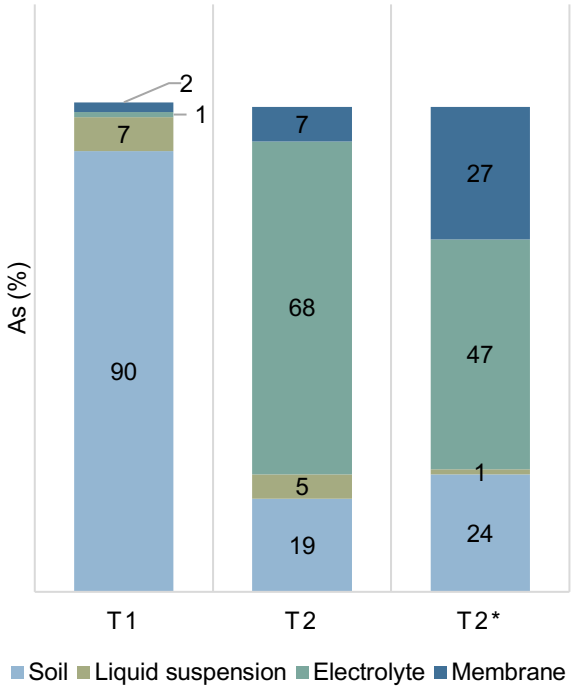
Treatment (T#)	Soil compartment	Electrolyte pH	Removal efficiency (%)	Mass balance (%)
T1	**Anode**	2	3	99
T2	**Cathode**	10	80	77
T2*	**Cathode**	10	81	96

*without pH adjustments

A weak As desorption from soil slurry in T1 was observerd due to cell-conditions (e.g. soil pH did not reach the ideal values for As desorption). According to the literature the desorption of As is highly dependent on both pH and redox potential as it influences the chemistry and composition of the As (Ottosen et al., 2000). The high As migration (74%) to anolye in T2 can be mainly explained by the desorption of As anions from soil to water.

The oxygen and carbon dioxide concentrations in suspended ED cell can be assumed to be in equilibrium with the atmosphere, which allows for oxidation of As (III) to As (V) as an oxyanion such as H2AsO_4^-, HAsO_4^{2-}or AsO_4^{3-}(Yuan and Chiang, 2008). In the case of T2, HAsO_4^{2-} is expected to prevail due to soil slurry pH (approx. 10-11) (Wang and Mulligan, 2006). This anion will migrate to anolyte through the AEM under the applied electric field. The ligand displacement reaction of hydroxyl ions with As species and high pH conditions prevent the re-adsorption of the metalloid (Jang et al., 2005). At low pH the occurrence of As anions is limited (pKa of As(V) is 2.2 and pKa of arsenite is As (III) 9.3). The main stable species in a reducing environment at neutral to acidic pH is the uncharged As(III) and since it is uncharged it is not mobile with electromigration (Ottosen et al., 2009).

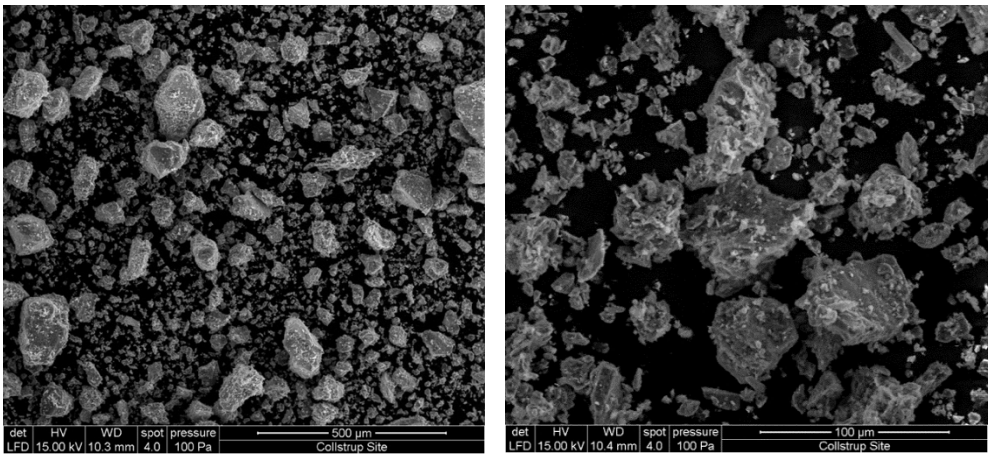
The alkaline conditions in anolyte favored the electromigration of As from soil compartment to electrolyte (Figure 3.4). Without pH adjustments in the electrolyte 27% of As got stuck in the membrane comparing with only 7% when pH adjustments in the electrolyte were performed. The results of As distribution in the different parts of the electrodialytic cell show that the electrolyte pH conditioning strategy is a way of maximise the As accumulation in electrolyte compartment, allowing a much more effective removal from the soil than without the anolyte pH conditioning strategy. The anolyte pH conditioning has rarely been studied and not with a soil slurry in ED cell and with higher periods of remediation. (Baek et al., 2009) showed that in a EK 3C-cell, catholyte conditioning with strong acidic solution and anolyte conditioning with strong alkaline showed similar As removals (62%), but with the double of the time of the operation (28 days) than the present study.



*without pH adjustments in the electrolyte

Figure 3.3 - Distribution of As in the different parts of the electrodialytic cell at the end of the experiments with acid (T1); basic (T2) pH cell-conditions and without electrolyte pH adjustments (T2*).

Changes in shape/morphology occurred in T2 where the suspended soil remained in cathode. Figure 3.4 shows the SEM analysis of soil particles before and after ED treatments. The results show that higher pH values may have influenced particles distribution. In T2, the small particles are adsorbed onto the surface of the largest ones forming aggregates (Figure 3.4 c)) whereas before ED treatment (Figure 3.4 a)) or in T1 (Figure 3.3 b)) the small particles are separated from the other particles.



a)

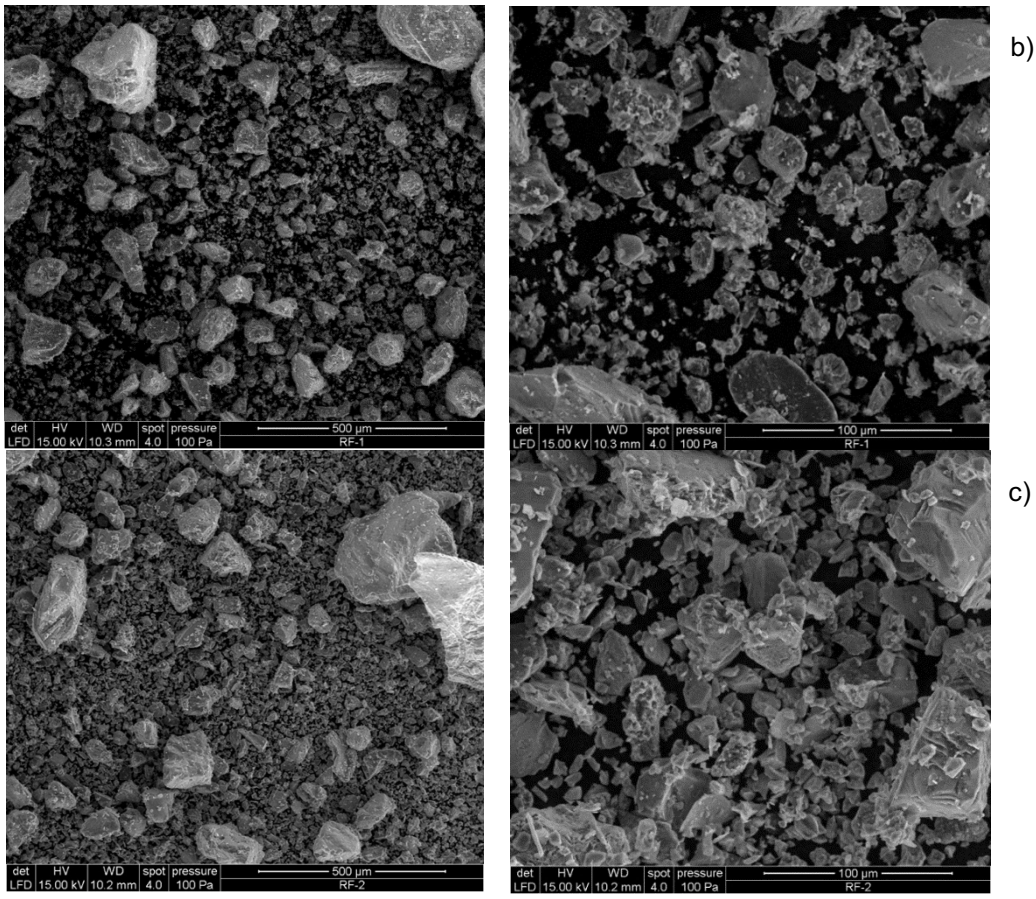


Figure 3.4 - SEM picture of Collstrop soil (a) before EDR; (b) after EDR treatments under acid, T1 and (c) alkaline conditions, T2.

3.1.2.3. Influence of time in ED removal

In order to make the ED process more efficient, the time of the treatment is an important parameter to be optimized. The final pH, conductivity and voltage drop for the experiments can be seen in Table 3.3. The pH of the soil slurry increased until 11 due to the OH^- generation in cathode compartment. The voltage decreased during the experiments due to the decreased in electrical resistance across the cell with the consequently increased of conductivity.

Table 3.3 - pH, conductivity and voltage in the ED experiments.

Soil code	Time (days)	pH_f	$Cond_f$ (mS cm^{-1})	$Volt_i$ (v)	$Volt_f$ (v)
Original	14	11.2	3.4	10.1	3.5
Original	7	11.1	1.2	10.8	6.6
Original	3	10.9	0.5	13.0	7.9

An overview of the As removals for the experiments is given in Figure 3.5. Around 10% more of As was removed from soil doubling the time of the experiment: 80% in 14 days; 72% in 7 days and 63% in 3 days. The results show that most part (63%) of the As was released from soil within 3 days and is slowly desorbed from soil over the time. Doubling the time of the experiment more 10% of As was removed from soil. However, for 14 days 30% more of As was found in electrolyte and less 19% in membrane comparing with 3 days. The presence of As in the membrane is not different when comparing the 14 and 7 days experiment (only 3% of difference), but 3 days did not show to be enough to migrate through the AEM towards anolyte. These results are promising because similar amount of As can be removed in short periods of time making the ED remediation more efficient.

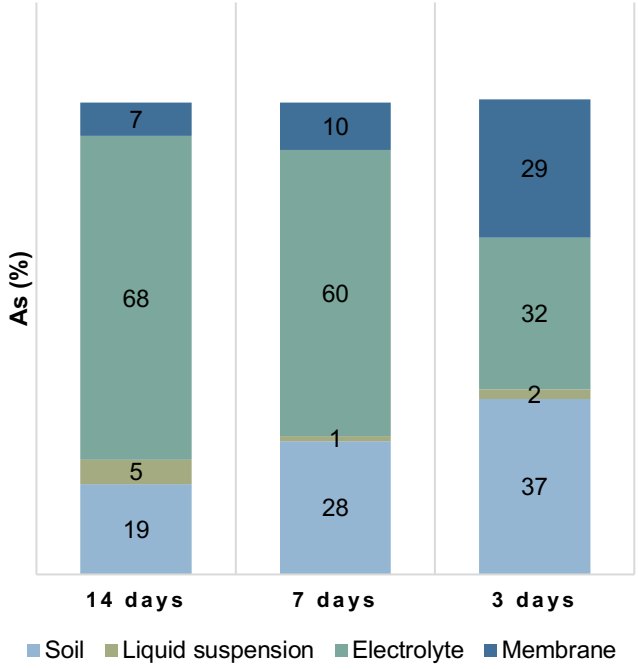


Figure 3.5 - Distribution of As in the different parts of the electrodialytic cell at the end of the experiments for 14, 7 and 3 days.

3.1.3. Combination of ED with pre-treated soil

3.1.3.1. General results

The desorption test (Figure 3.6) showed that most part of the As (>80%) is desorbed from soil (original or pre-treated) either under highly acid 0.1<pH<0.4 and alkaline pH values pH>12.

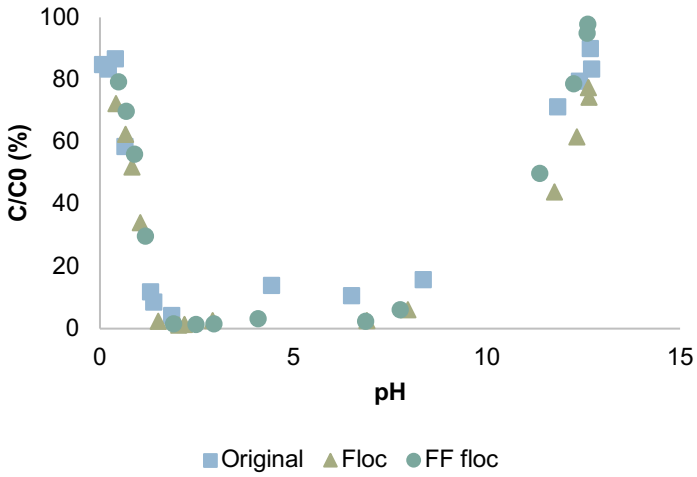


Figure 3.6 - Desorption dependency on pH of As in original soil, washed ("Floc") and the fine fraction from washed soi ("FF floc").

The voltage and conductivity behaviour are shown in Figure 3.7 and 3.8, respectively. The conductivity increased until the end for all the experiments due to the addition of OH^-. The voltage behaviour is concordant to the conductivity results. "FF floc" experiments had higher voltage comparing with the other experiments because less ions were released and the electrical resistance across the cell increased. The feasibility of the conditioning anolyte with strong basic solution was studied by (Kim et al., 2009) and (Baek et al., 2009b) and less energy expenditure was registered comparing without pH adjustments. This fact shows to be an advantage for EDR as energy consumption is a critical factor to evaluate the feasibility of EDR.

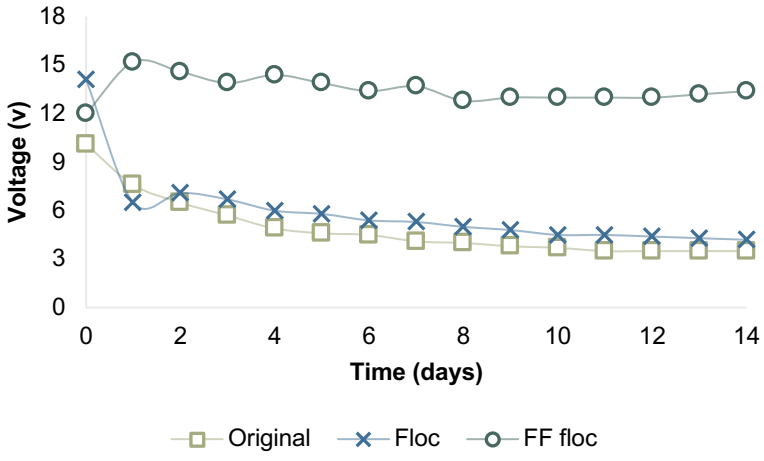


Figure 3.7 - Voltage over the cells during the EDR.

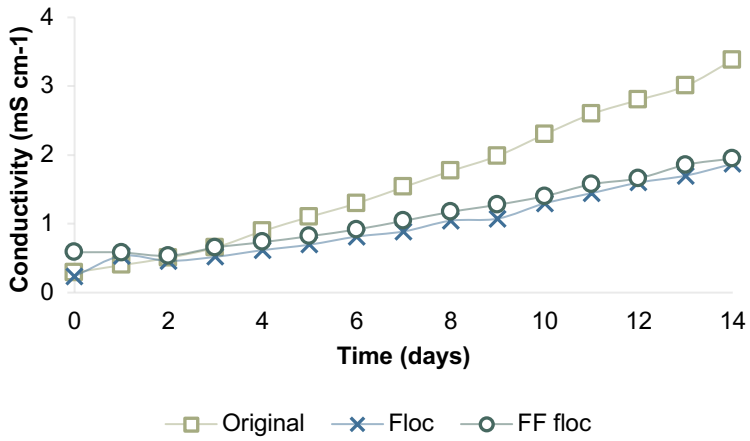


Figure 3.8 - Conductivity variation in the soil slurry during the ED treatment.

3.1.3.2. As removal

An overview of the results obtained in the ED experiments is given in Table 3.4 and the distribution of As in the different parts of the electrodialytic cell at the end of the ED experiments is in Figure 3.9.

Comparing the removals between the three soils, the amount of As removed from original soil was higher (>20%) and mostly recovered in the electrolyte (68%) when comparing with the pre-treated soil (51% and 37% of As in electrolyte). Even though, the concentration of As showed to be statistically (p<0.05) higher in washed and fine fraction, higher As removals were not achieved.

Table 3.4 - Overall results of EDR experiments comparing bulk and pre-treated soil.

Soil code	Initial amount of As (mg/kg)	As removal from soil [1] (mg/kg)	As removal from soil [1] (%)	Mass balance (%)
Original	594 ± 79	475 ± 4	80	77
Floc	784 ± 10	478 ± 2	61	94
FF floc	804 ± 4	400 ± 10	50	81

[1] Removal was calculated as the sum of As found in electrolyte, membrane and liquid suspension.

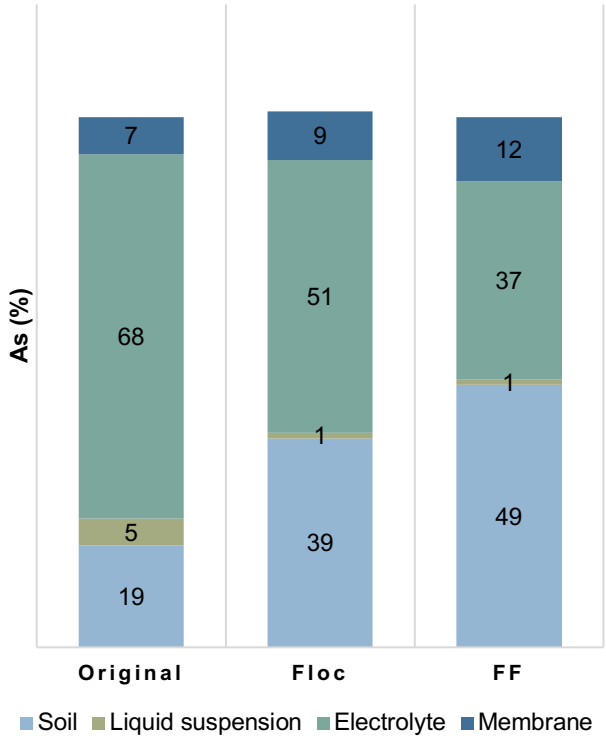


Figure 3.9 - Distribution of As in the different parts of the electrodialytic cell at the end of the ED experiments.

The binding strength between soil particles and As before and after EDR was analyzed by sequential extraction (Figure 3.10). The results show that As was mainly associated with the exchangeable and reducible phases (more mobile fraction) before remediation for the three types of soil. However, should be noticed that oxidizable fraction was higher for the pre-treated soil. After EDR, most part of the As in the exchangeable fraction was removed during EDR, with the less available fractions (oxidizable and residual) increasing mainly for the pre-treated soils. This proves that removing As from original soil it might be easier because As is preferentially bound to Fe and Mn oxides (reducible fraction), instead of oxidizable (large fractions of sulphides) and residual fractions, which is reported to be more difficult to remove (Kim et al. 2001).

The optimization of the washing soil step may potentially increase the EDR efficiency as in theory, after washing less soil needs to be treated and consequently less remediation costs. More laboratorial studies are required in order to study the effects of flocculant addition in soil washing.

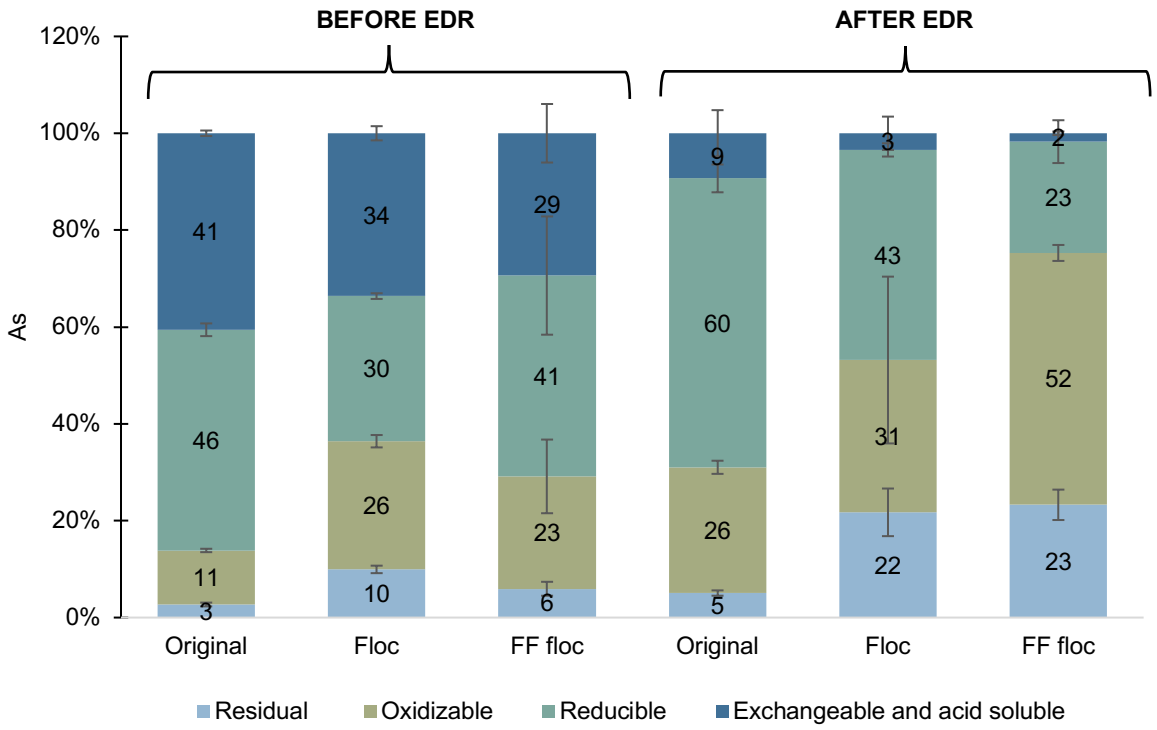


Figure 3.10 - Distribution of As in the different fractions of the soil (original soil, washed and fine fraction) before and after EDR experiments analyzed by sequential extraction method (n=2).

3.1.4. Reuse of soil in building materials

Even after EDR the values of As were still above regulation. In this sense, a different alternative to the soil disposal was tested. Figure 3.11 shows the brick pellets for building materials purposes made with different amounts (%) of the original soil. Due to the insufficient particle aggregation observed in pellets constituted by 100% of treated soil, clay was joined at different amounts (50%, 75% and 90%). Clay minerals brought plasticity to the bricks showing consistence for all the tested percentages (50, 75 and 90%). Also, the brick pellets showed a different appearance (e.g. color) in accordance to the amount of clay.

The suitability of the brick pellets to be used as a construction material was defined by porosity, density and As leachability (Table 3.5).

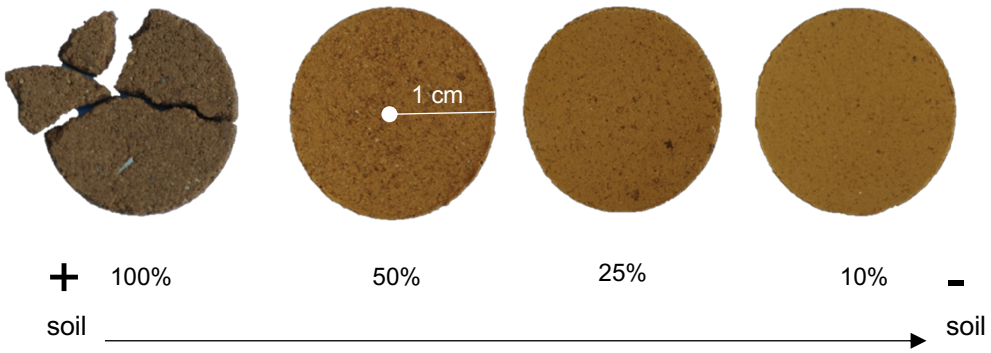


Figure 3.11 - Brick pellets with different amounts of soil (100 %, 50 %, 25 % and 10 %).

Porosity, which is directly related to the amount of water present, increased (between 27% to 34%) with the addition of clay to the brick pellets. This is explained by carbonates that decompose during sintering with gas releases conducting to pore formation in bricks (Chen et al., 2016).

Higher amount of pores means higher water absorption, which can reduce the brick resistance and durability. Regarding to dry matter density, the bricks showed to be very similar.

Leaching tests proved that As present in EDR treated soil was not released from the bricks. That means the use of treated soil as building material does not represent a risk to the environment, open a path to use this soil also for construction materials without risk of As leachability.

Table 3.5 - Brick pellets parameters (mean ± SD).

Parameters	**Amount of soil (%)**		
	50	25	10
Porosity (%)	27 ± 1	32 ± 1	34 ± 1
Density (mg m^{-3})	2.6 ± 0.1	2.7 ± 0	2.7 ± 0.1
Leaching (mg kg^{-1})	ud	ud	ud

ud: under value

3.2. Petroleum hydrocarbons removal from soil

3.2.1. Soil characteristics

The soil characterization is shown in Table 3.6. The soil had a a sandy loam texture, which allows a good drainage, with a neutral pH (7.43) both low buffer capacity (low content of carbonate, 1.9%) and organic matter (4.4%).

The soil did not show to have lack of nutrients through the P, K, N analysis. The concentration of metals found in the studied soil were below to the limit values in soils in Denmark. However, the presence of Cu (43 mg kg^{-1}), Pb (37 mg kg^{-1}) and Zn (85 mg kg^{-1}) suggests anthropogenic sources. The metals Fe

and Al were the most abundant metals found in the soil sample (12702 and 5410 mg kg^{-1}, respectively). This aspect is important as soluble iron compounds, such as Fe^{2+}, are known to play an important role in the degradation of organic compounds by reacting with OH radicals. Even though, the concentrations of metals are below limiting values, their monitoring after EKR is important as the pH changes may promote ions migration.

Regarding TPHs, the studied soil showed a contamination of 69 500 ± 500 mg kg^{-1} being 100 mg kg^{-1} the quality criteria for soil in areas with very sensitive land use in Denmark (Danish EPA, 2015). In terms of the type of the contamination, Figure 3.12. shows a chromatogram obtained for the soil extraction where is possible to see that it mainly contains medium-molecular weight compound mixtures.

Table 3.6 - Sisimiut Soil characteristics.

Characteristic	**Value**	**Unit**
pH	7.43 ± 0.02	
Conductivity	574 ± 75	µS cm^{-1}
Chloride	3074	mg kg^{-1}
Carbonate	1.9	%
Organic matter	4.4 ± 0	%
Water content	10	%
Grain Size		
Clay	4.40	%
Silt	47.4	%
Sand	48.2	%
Metals and elements		mg kg^{-1}
Al	5410 ± 502	
As	1 ± 0	
Ca	8082 ± 775	
Cd	0 ± 0	
Cr	22 ± 1	
Cu	43 ± 11	
Fe	12702 ± 8998	
K	1820 ± 154	
Mg	3661 ± 279	
Mn	116 ± 9	
Na	613 ± 41	
Ni	26 ± 16	
P	770 ± 54	
Pb	37 ± 5	
S	1653 ± 177	
Zn	85 ± 19	
Oil		mg kg^{-1}
TPH	69500 ± 500	

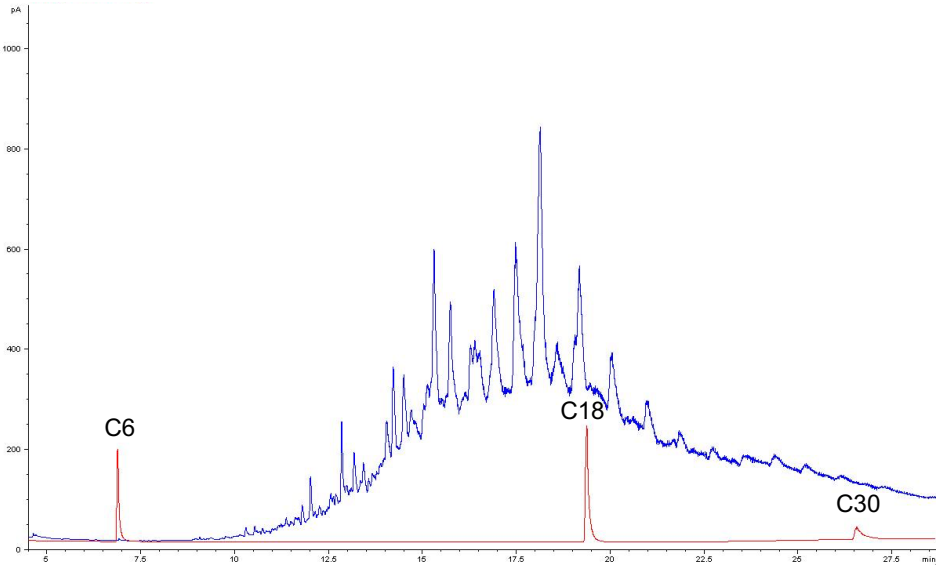


Figure 3.12 - Chromatogram obtained from the initial soil extraction and internal standard (monobrobenzene, C6; o-terphenyl, C18 and squalan, C30).

3.2.2. General results

Aiming to minimize environmental disturbance, it is important to monitor the soil characteristics after EKR. The parameters analysed after the experiments are found in Table 3.7. After application of a continuous electric field, due to the electrolysis of water, the pH became more acidic and alkaline in anode and cathode, about 6.9 and 10.9, respectively. When the polarization was changed, it prevented the acidification and alkalization due to shifting fronts counteracting each other. For the EKR experiments where the current was switched On/Off, the soil pH only changes in the anode side probably due to oxidation reaction that generates H^+ faster than OH^-, and/or precipitation of hydroxides.

The initial values of voltage were similar among the experiments and ranged from 17.2 to 23.2 V. Over the time, voltage values fluctuated, including high levels of voltage (40 V). For REP, slight oscillations in the value of the voltage corresponde with the daily change in the polarity of the electric field. In general, all changes were a consequence of the changes promoted in the soil characteristics, which can be explained in terms of an electrical resistance increase of the soil matrix related with the water evaporation during the day. Even though the experiments were weighted once a day and water was added if needed, during the day the water can evaporate reducing the moisture content and decreasing the soil conductivity.

The conductivity increased when continuous current was applied (except in cathode side under cold temperature). This might be associated to the significant increase in the proton and hydroxyl ions concentrations as a consequence of the electrolysis of water. When applying REP, the conductivity did not increase because the acid and basic front are partially balanced. Similar results were showed by Barba et al. 2017 (Barba et al., 2017).

Regarding organic content, no differences were found between controls and EKR experiments, suggesting that the current did not have any effect in organic matter degradation.

The SEM analysis did not show differences between controls and EKR experiments regarding to physical characteristics (Figure 3.13).

Table 3.7 - pH, conductivity and organic content and after EKR.

Temperature	Current strategy	Electrode polarity	pH	Conductivity (µS cm^{-1})	Organic content (%)
Room	Continuous	Anode	6.9	489	2.8
		Cathode	10.9	446	2.7
	REP	Anode/cathode	7.7	296	3.0
		Cathode/Anode	8.0	200	2.8
	On/Off	Anode	7.8	376	2.6
		Cathode	10.8	335	2.8
	Control*	*NA*	8.0	311	2.7
Cold	Continuous	Anode	7.2	455	3.0
		Cathode	10.8	267	2.7
	Control*	*NA*	7.9	256	3.2

*without applied electric current
NA = not applicable because the experiment run without current.

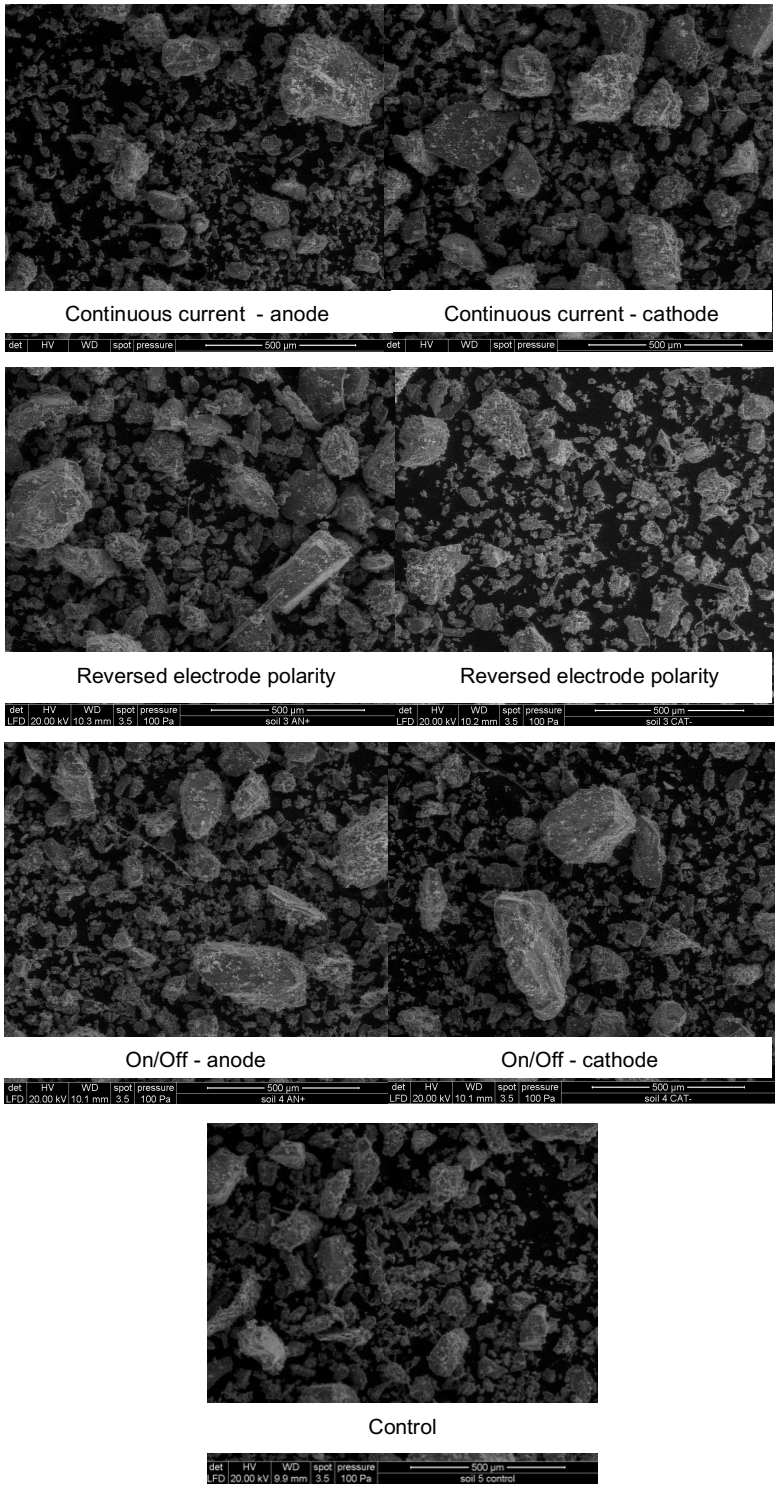


Figure 3.13 - SEM analysis of Polar soil before (control) and after EKR experiments in the different soil sections (anode and cathode).

3.2.2. Metals and other elements after ED soil remediation

Comparing with the initial values (Table 3.8), the metals and other elements concentration either in anode and cathode did not significantly change (without statistical differences). The values are shown in Table 3.8. The experimental conditions did not promote the metals and/or nutrients migration in the natural soil matrix towards anode or cathode, suggesting low mobility / bioavailability or low treatment time to promote effective migration. This result can be justified with the soil pH that did not change to very low (pH<4) or high values (pH>11), values that have been reported for the metals to have mobility (Bennedsen et al., 2012).

Table 3.8 - Average (n=2) of the metals and elements (mg kg^{-1}) found in Sisimiut soil before and after EKR experiments.

			Al	Ba	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Zn
	Initial values		5410±502	78±6	8082±775	0	22±1	43±11	12702±898	1820±154	3661±279	116±9	613±41	26±16	770±54	37±5	1653±177	85±19
Room temperature	Continuous	Anode	5362±247	96±9	7843±213	-	21±2	42±2	12785±890	1169±45	3334±209	129±9	592±65	21±1	783±44	65±19	927±98	90±30
		Cathode	1852±495	93±12	14237±6754	-	24±1	41±2	13725±7189	1351±136	3943±275	154±21	519±61	20±2	791±56	51±2	728±13	69±1
	REP	Anode	4913±521	88±3	8761±1133	-	20±3	34±4	12475±581	1190±14	3254±224	141±6	504±42	26±6	619±64	48±2	801±125	58±1
		Cathode	4734±433	89±8	11789±439	-	20±1	38±1	11556±497	1194±81	3259±263	127±6	524±12	19±0	732±33	62±4	640±13	65±7
	On/Off	Anode	4718±202	88±6	12209±1653	-	20±1	39±4	12269±613	1133±83	3192±67	133±11	525±110	22±3	647±112	61±7	663±25	72±1
		Cathode	4547±269	88±8	12393±384	-	18±1	35±3	10945±25	1196±71	3043±137	120±3	519±50	20±0	577±67	-	688±137	61±3
	Control		4562±119	98±15	11046±941	1±0	19±2	35±1	11297±72	1126±71	3280±306	124±0	490±50	18±1	665±32	52±1	685±79	63±6
Cold temperature	Continuous	Anode	5234±472	85±10	9534±2066	1±0	20±4	36±4	11502±702	1190±8	3120±90	119±8	535±11	17±2	812±22	47±12	836±55	64±8
		Cathode	4514±45	86±9	12376±360	-	21±2	34±2	11093±446	1155±44	3130±60	121±3	494±81	20±3	818±253	80±35	590±125	76±14
	Control		4698±55	84±1	11801±382	-	22±2	36±2	12323±894	1109±2	3272±58	130±6	486±5	19±1	727±43	95±49	745±150	101±48

3.3.3. Petroleum hydrocarbons removal by EKR

Overall reductions up to 75% of TPHs were observed. The Figure 3.14 shows the remediation percentages after EK treatment comparing with the initial soil sample.

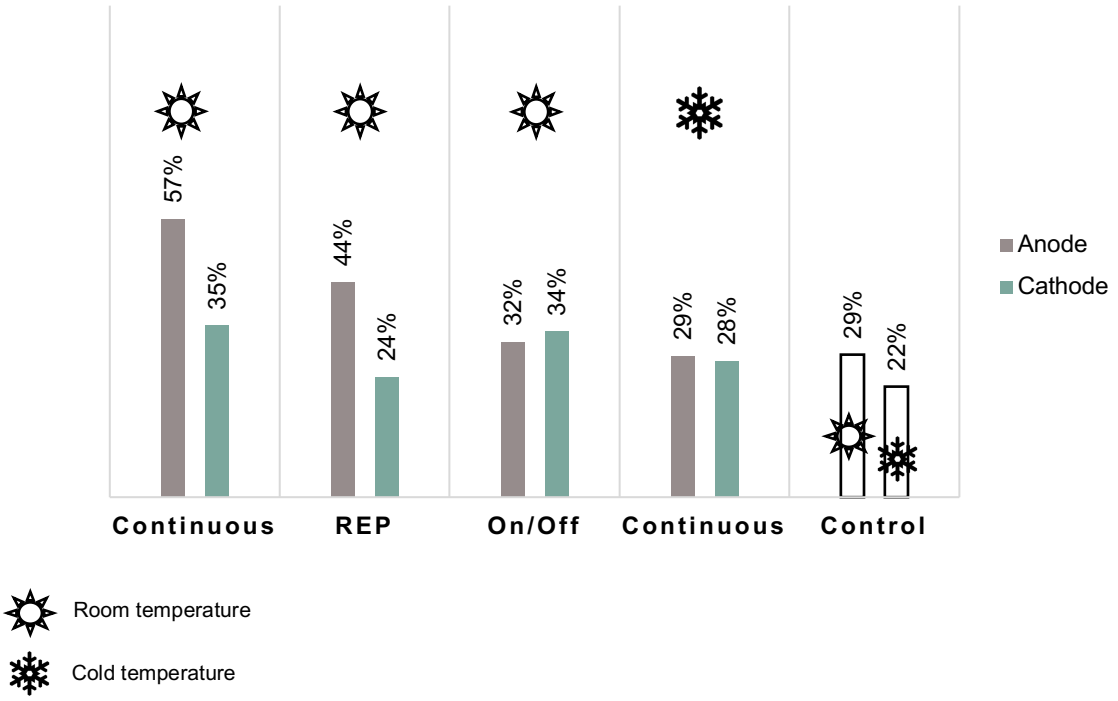


Figure 3.14 - Presence of TPHs after EKR (either in anode and cathode) comparing with the initial soil (control).

- *Controls at room and cold temperature*

Comparing the initial TPHs concentration with both controls (without current) it is possible to attribute loss of TPHs to either bio or abiotic factors. Hydrocarbons odours were felt during the experiments suggesting that volatilization occurred, although air samples were not collected. In addition to volatilization, the presence of indigenous cold-adapted microorganisms that persist in contaminated soils showed to have influence in oil degradation and have been study by several authors e.g. (Aislabie et al., 2006).

Comparing both controls, at room and cold temperature only slight differences on TPHs remediation were found (29% and 22%, respectively). This suggests that temperature did not influence in oil degradation when current was not applied. In literature, the effect of temperature in the microorganisms is not linear but has been reported to have a great influence in biodegradation (Mena et al., 2016). In the case of hydrocarbons biodegradation, the temperature directly affects the chemistry of the compound, as well as, the physiology and diversity of the microbial flora in the contaminated matrix. Some studies have demonstrated that hydrocarbons mineralization occurs in soils at low temperatures, however, the rate and perhaps the extent of degradation are higher at elevated temperatures and thus the bioremediation levels are lower in cold temperatures (Aislabie et al., 2006). However, some studies have proven higher removals under cold than higher temperatures e.g. (Sanscartier et al., 2009). With

electro-based technologies, (Pedersen et al., 2017) showed that PCB removal by ED process was more efficient at low temperatures, which was attributed to the naturally occurring PCB degrading microbial communities not being adapted to higher temperatures. In the present study, even though no significant differences were found between controls (no current) at different temperatures, when current was applied current some differences were found.

- *DC current applied*

Comparing with controls, EKR itself did not improve the oil remediation for the tested conditions, but some differences were seen among experiments.

Comparing both (room and cold temperature) the experiments with continuous electric current, approx. 30% more remediation was achieved under cold temperature in anode side. This difference can be related with (i) microbial activity inactivation in anode under room temperature and (ii) due to electroosmotic flow. Through the controls (without applied current) seems like natural attenuation had an important role in TPHs degradation. The influence of applying an electric field on microbial communities is not completely explored yet but some studies reported a limited effect (Mena et al., 2016) or more pronounce effect, stimulating microbial activity (Shi et al., 2008). However, chlorine and hydrogen peroxide generated in secondary electrode reactions may inhibit microbial communities adjacent to the electrodes (Gill et al., 2014). In this sense, the type of current applied can be crucial in the soil remediation by microorganisms, e.g. Ramírez et al. (2015) (Ramírez et al., 2015) state that biological treatment could be improved by the use of electrokinetic soil flushing, but only by using the REP.

Similar to continuous electric current at room temperature, the REP also showed 20% of difference between anode and cathode side in terms of TPHs presence (44% vs. 24%, respectively). The soil temperature was not measured during the experiments because low current intensity (5 mA) was applied and no large changes in soil temperature were expected (Esperanza Mena et al., 2016). However, it is important to mention that anode side in these experiments was drier and differences in anode and cathode are probably attributed to the electrical heating as a consequence of the ohmic drops, which could lead to microbial inactivation (Barba et al., 2017; Ramírez et al., 2015). This result can be corroborated comparing the TPHs presence in soil at room and cold temperature applying continuous current (57% *vs.* 29% of TPH presence in anode at room and cold temperature, respectively). The temperature influences oxygen solubility and reduces the metabolic activity of aerobic microorganisms. In REP, differences between anode and cathode remediation were also found, but heating is not expected to be the reason (Barba et al., 2017). The differences can be attributed to the electroosmotic flow, which was found to decrease with the REP frequency making the microbial distribution in soil not uniform (Barba et al., 2017). Further studies should optimize the REP strategy testing different periods of time.

When On/Off was applied no differences were verified for TPHs remediation in anode and cathode (68% and 66%, respectively). The effect of heating in anode side was probably avoided whit the Off

current periods. In addition, the Off period allows a lower energy expenditure because half of the time the current was applied.

In the present work, the tested conditions did not show the effect of current in oil remediation due to the contaminant's characteristics. For in situ EK remediation there is no need for soil excavation and transportation, however longer treatment times may be required regarding recalcitrant contamination, as the TPHs in the present study showed to be.

Having in mind the characteristics of the artic environment, the remediation technology developed must operate under challenging environmental conditions, be easy to operate, have low energy requirements, and have minimal impact on the environment. In addition, it is important to keep the soil and experimental conditions (such as pH and electrical conductivity) within proper values for microbial life. In this sense, the REP contributed to make less changes undergone by the soil as a consequence of the electrolysis of water, because they are partially balanced in each polarity reversal. In addition, in theory, the REP favours the homogenization of the system at microscopic scale as it acted as a mixer which put in contact pollutants, microorganisms and nutrients (Esperanza Mena et al., 2016). A combination between REP and On/Off could be a strategy to test together in order to optimize the EKR: less energy spend with less changes in soil characteristics.

3.4. EOC removal from soil

3.4.1. Influence of the cell design

3.4.1.2. General results

The pH, conductivity and voltage measurements along the experiments are in Figure 3.15, 3.16 and 3.17, respectively.

- *pH*

Comparing the three cell designs the soil slurry pH underwent some variations.

The controls (without applied current) showed no differences between the initial and the final pH for soil slurry and electrode compartments (anode and cathode). In the experiments with applied current, the pH decreased over time in the anode compartment (from pH ≈ 5.5 to pH around 2) due to the formation of H^+ and increased (pH > 9) in cathode due to the generation of OH^-.

Concerning the slurry soil pH, for 1C-cell, no significant differences were found (p<0.05) comparing the initial (pH 5.1 ± 0.5) and the final (pH 5.5 ± 0.1) soil pH. This result means that the production of H^+ and OH^- at the electrodes were balanced.

In the 2C-cell, the soil slurry pH increased till 9.60, which is higher than the pKa of the EOC under study. This means that the three contaminants were in their ionized form contrary to the other cells designs. It should be noted that the slightly lower pH in the cathode compartment of the 2C-cell experiment, comparing to the 3C-cell, might be explained by the electromigration of some OH ions towards the anode compartment, as well as due to the soil buffering capacity. For 3C-cell the soil slurry (central

compartment) slightly decreased (from 4.74 ± 0.61 to 3.55 ± 0.26), which is explained by the passage of H^+ from the anode compartment to the central compartment through the AEM, as well as due to the water splitting at the AEM in the central compartment. As already referred, the AEM is not 100% ideal and thus some of the acid generate at the anode might pass to the soil slurry (Ottosen et al. 2000).

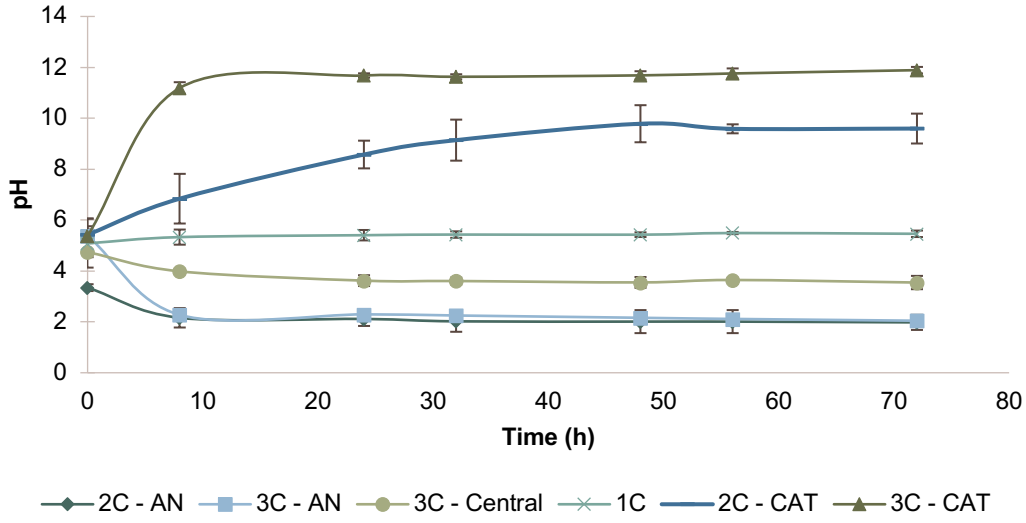


Figure 3.15 - pH variation with time in the different compartments for the three designs of cell: 3C-, 2C- and 1C-cell.

- *Conductivity*

The slurry soil conductivity in 3C- and 2C-cell decreased 8 and 4 times, respectively, within the first 8 h of experiment. This represents a quick depletion of free ions from the solution towards the electrode compartment (s), where the conductivity increased. In the 2C-cell, the soil slurry had the highest final conductivity (3 times more; 2C vs. 3C-cell; 0.17 mS cm^{-1} vs. 0.06 mS cm^{-1}). This may be explained by the 2C-cell set-up design as only the ions with negative charge are removed from the slurry soil, towards the anode compartment, with all the positive ions remaining in solution. In the 1C-cell the conductivity remained constant during the experiment meaning no mobilization of ions towards another compartment.

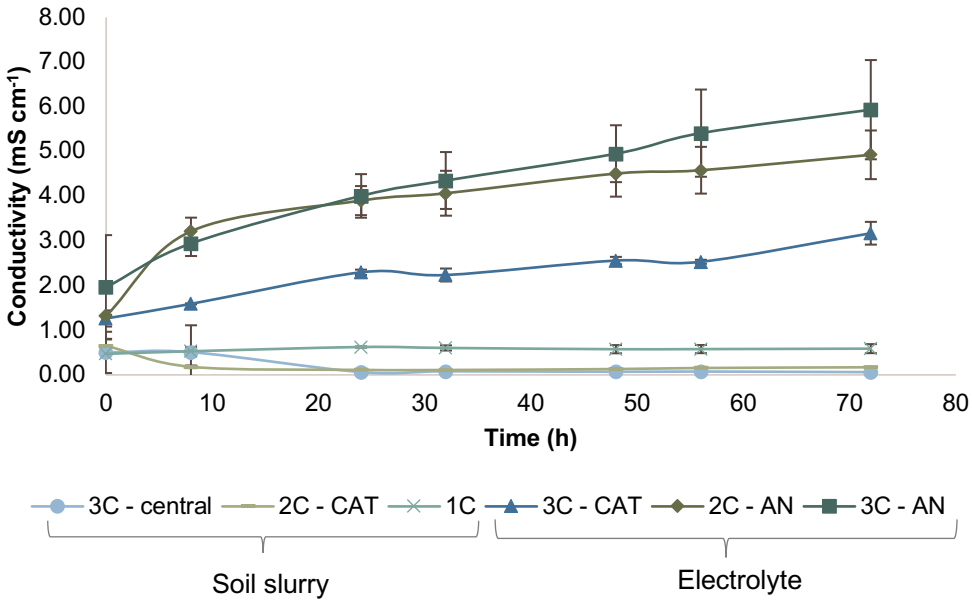


Figure 3.16 - Conductivity (mS cm^{-1}) variation with time in the different compartments for the three cell designs (3C, 2C and 1C).

The conductivity experimental data is in accordance with the voltage behavior (Figure 3.17). In the experiment with 1C-cell, the voltage was constant (≈14 V) as the ions were not being removed from the soil slurry (resistance did not change (1444 Ω)). For the experiments with electrode compartments separated by ion exchange membrane(s) (2C- and 3C-cell) the voltage had a logarithmic shaped growth with a quick rise in the first day, then slightly decreased and remained constant until the end of the experiments.

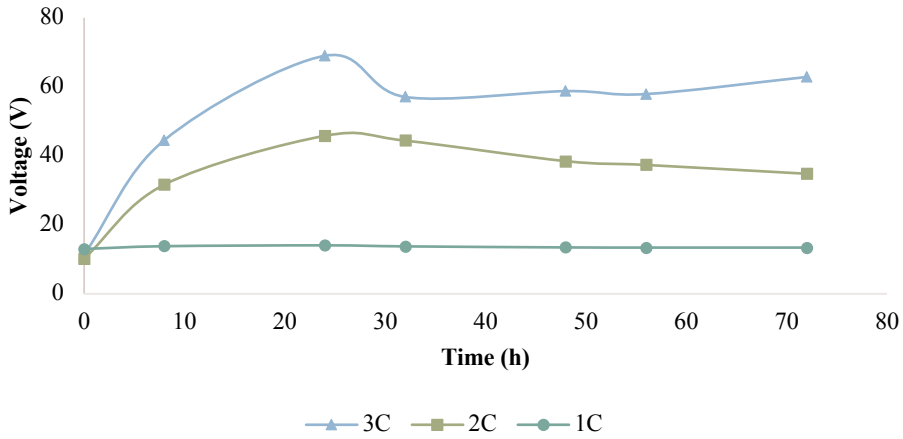


Figure 3.17 - Variation of voltage with time for the three different designs of cell: 3C, 2C and 1C.

In 3C-cell design none of the electrodes were placed directly into the soil slurry but into an electrolyte solution separated by ion exchange membranes. This resulted in a higher increase of the resistance till the end of the experiment comparing with 2C-cell (5.7 times vs. 3.5 times) due to the higher depletion

of ions from the soil slurry (Table 3.9). The 2C-cell was expected to have lower resistance than the 3C-cell since the set-up only consisting of two compartments separated by AEM, where the electrolysis reaction at the anode results in a higher conductivity of the soil slurry at the end of the experiment (0.17 mS cm^{-1} vs. 0.06 mS cm^{-1}; 2C vs. 3C-cell). This also results in a lower potential energy (W) between the two electrodes for 2C when comparing with 3C-cell (0.100 to 0.350W for 2C, and 0.132 to 0.7546 W for 3C). The values are shown in Table 3.9.

Table 3.9 - Current, voltage, resistance and power for the three cells design tested for EOC removal from slurry soil.

Cell-design	I (A)	V_i (V)	R_i [1] (Ω)	P_i [2] (W)	V_f (V)	R_f [1] (Ω)	P_f [2] (W)
3C	0.012	11	917	0.132	63	5250	0.756
2C	0.010	10	1000	0.100	35	3500	0.350
1C	0.009	13	1444	0.117	13	1444	0.117

Legend:
I - current intensity (A, Amps)
V - voltage (V, Volts)
R - resistance (Ω, Ohm)
P - power (W, Watts)
i = initial
f = final
According with Ohm's law:
[1] V = I * R
[2] P = V * I

3.4.1.3. EOC removal from soil slurry

The three EOC selected for the present study were BPA, EE2 and MBPh.

At the end of the experiments, the difference between the amount of contaminants detected in the cell (through mass balance calculations) and their initial amount, was expressed as the percentage of contaminant removed from the soil compartment either by degradation and/or mobilization (through electromigration) towards the electrode compartment(s). The results are shown in Table 3.10.

- *Controls (without applied electric current)*

The experimental results from control set-ups, without applied current, showed differences among contaminants removals (ranging from 23% to 61%) in the slurry soil compartment with EOC not being detected in the electrode compartment(s). These removals may be attributed to biotic and abiotic processes that may have occurred along the 3 days of experiments, although no biological analysis was carried out in this study. This hypothesis is supported by previous studies which have shown that degradation of EOC in soils is part due to microbial activities (Xu et al., 2009). Additionally, comparative experiments conducted in sterilized soils carried out by (Yu et al., 2013) showed that the sterilization treatment resulted in a decrease of the degradation rates of PPCPs indicating that microbial activity played an important role in degradation.

- *DC applied*

  - *Comparison among cell designs*

When electric current was applied the removals of contaminants were improved, with removals from 9% for MBPh to 84% for BPA, with differences among the tested cell-designs.

The 3C-cell design presented more than 75% of removal, which consists in mobilization and degradation from soil slurry. However, although removals are similar in the soil slurry, compounds showed different behaviors inside the system. BPA and MBPh were mainly mobilized and thus detected in the anolyte (83% and 50%, respectively), showing low degradation rates (0% and 13%, respectively). On the other hand, EE2 was not detected in any of the electrolytes and suffered 84% of degradation from soil slurry.

The 2C-cell design achieved more than 68% of removal (mobilization and degradation) from soil slurry for the three contaminants. Similar with the 3C-cell, BPA was mainly detected in the anolyte (>80%). EE2 and MBPh presented higher degradation rates (84% and 62%, respectively). The 2C-cell design improved the degradation of MBPh when comparing with 3C-cell (62% vs. 13%, $p < 0.05$). This means that when the soil is placed in the cathode compartment MBPh degradation is improved, and when placed in the middle cell compartment it is mobilized to the anode compartment (50%) decreasing its degradation.

In the 1C-cell design, the removal does not imply contaminants mobilization but electro-degradation due to oxidation and reduction reactions at the electrodes. The contaminants were removed from soil slurry following the order: EE2 (66%) > BPA (61%) > MBPh (44%). The absence of separation compartments gives a more similar removals among the three EOC tested. Its experimental results, in opposition to the other tested cell designs, showed to improve the BPA degradation (61%) as no mobilization was present. On the other hand, at the end of the experiments, 39% of BPA was still detected in soil slurry, being higher than in the other cell designs 3C (17%) and 2C (16%) even though without statistical differences ($p > 0.05$). Significant statistical differences ($p < 0.05$) were only observed for MBPh between 3C- and 2C-cells *versus* 1C-cell.

  - *Comparison among EOC*

The differences on EOC behavior regarding to their degradation may be attributed to both (i) the different chemical structures and (ii) degradation mechanisms.

The contaminants under study are considered hydrophobic with similar Log K_{ow} ($3.32 < \text{Log } K_{ow} < 3.82$). However, the EE2 has the lowest solubility (11.3 mg L^{-1}) when comparing with BPA and MBPh (69 and 120 mg L^{-1}, respectively), which has influence in compounds mobilization, and consequently their degradation rate.

The fact that soil was in a suspension, play an important role on the desorption of the compounds and their consequently mobilization attributed to the creation of larger interaction surfaces between soil and EOC that increase their dissolution helping to release the compounds that are bounded to the soil

fraction. The stirred set-up has been shown to significantly increase removal efficiencies of other contaminants such as heavy metals e.g. (Kirkelund et al., 2009).

In addition, in soil suspension the pH is easily changed, which showed to be an important parameter in MBPh degradation/removal, as it increases the contaminant solubility. Ionizable chemicals, depending on their pKa and on the medium pH, are converted to either cations or anions. When pKa > pH compounds the neutral species are predominant. In 2C-cell, the pH of the soil slurry compartment was 9.14 ± 0.81 after 24 h, meaning that MBPh was in its ionized form (pKa = 7.6; pKa < $pH_{soil\ slurry}$). MBPh suffered deprotonation becoming more soluble and being able to migrate from the cathode towards the anode compartment through the AEM, where it may suffer anodic oxidation. The faster mobilization of the MBPh in the 2C-cell comparing to the 3C-cell may explain the differences between the amount of MBPh detected in the anode compartment of the 2C-cell (6%) comparing to the 3C-cell (50%): the faster mobilization resulted in a higher residence time in the anode compartment and, consequently, more time to suffer anodic oxidation. This hypothesis is supported by the degradation rates of MBPh at the end of the experiments: 62% in 2C-cell vs. 13% in 3C-cell. For BPA the pH effect was also noticeable. In the 2C-cell the BPA pKa < $pH_{soil\ slurry}$ may have contributed to the higher BPA mobilization towards the anode compartment (>10% comparing with the 3C- cell). The effect of pH on compounds removal has been studied by other authors, e.g. Nam et al. (2014) (Nam et al., 2014) confirmed that EOC behavior vary from compound to compound and are difficult to predict, because is often controlled by interactions with specific functional groups or complex pH-dependent speciation.

- *Final remarks*

Among the three different cell-designs tested, the effect of electric current on EOC removal comparing with controls showed to be similar for both 3C- and 2C-cell: BPA (≈84%)>EE2 (≈35%) > MBPh (≈10%). The results with the 2C- and 3C-cells show that BPA had a high mobilization rate with more than 83% in the anolyte in the end of the experiment. On the other hand, the 1C-cell promoted by 60% of BPA and E2 degradation, and by 20% for MBPh. The use of a cell with compartments (3C- and 2C-cells) only increased the removal of BPA in approx. 20% through mobilization. These findings support that the absence of cell compartments enhance the degradation of the compounds in the soil slurry. The homogenous degradation of the three contaminants in the 1C-cell (removals from 44% to 66%), comparing to the other tested cell designs, may be attributed to the presence of both cathode and anode electrodes in the soil slurry compartment, thus promoting both reduction and oxidation reactions.

Table 3.10 - Percentage of contaminant (BPA, EE2 and MBPh) detected in the different cell compartments and degraded, at the end of the experiments in relation to the initial amount (n=2).

Cell-desing	Cell-compartment	EOC					
		BPA		EE2		MBPh	
*Control-3C	Soil slurry (central)	100	sd	52	sd	36 [d]	± 17
	Anolyte	< LD	0	<LD	0	3	sd
	Catolyte	< LD	0	<LD	0	<LD	0
	Degradation	**0**		**48**	**sd**	**61**	**± 17**
3C	Soil slurry (central)	17 [a]	± 4	16	± 9	25 [c, d]	± 9
	Anolyte	**83**	± 6	<LD	0	**50**	sd
	Catholyte	<LD	± 0	<LD	0	13	sd
	Degradation	**0**		**84**	**± 9**	**13**	**± 9**
*Control-2C	Soil slurry (cathode)	100	sd	50 [d]	sd	40 [d]	± 12
	Anolyte	<LD	sd	<LD	sd	2	0
	Degradation	**0**	**sd**	**50**	**sd**	**58**	**± 12**
2C	Soil slurry (cathode)	16 [a]	sd	16	sd	32 [c, d]	± 14
	Anolyte	**100**	± 20	<LD	sd	**6**	± 1
	Degradation	**0**		**84**	**sd**	**62**	**± 15**
*Control-1C	Soil slurry	100 [b']	± 20	100	± 20	77 [d]	± 35
	Degradation	**0**		**0**	**0**	**23**	**35**
1C	Soil slurry	39 [a, b]	± 30	34	sd	56 [c', d]	± 10
	Degradation	**61**	**± 30**	**66**	**sd**	**44**	**± 10**

Legend:
*without applied current
<LD: Below detection limit; sd-without standard deviation;
x and x' mean statistically differences ($p<0.05$) comparing:
[a]BPA present between cells design (3C, 2C and 1C); [b]BPA for each cell design and respective control; [c]MBPh between cells design (3C, 2C and 1C); [d]MBPh for each cell design and respective control.

3.4.2. Electrokinetic process applying different current strategies

3.4.2.1. General results

- *pH*

The results of soil pH are in Figure 3.18. The soil presented an initial pH of 6.23 ± 0.02 and after the control experiment (7 days without electric current) soil pH was 6.48 ± 0.04 without statistical differences ($p>0.05$). After application of a DC field it is expected that soil pH changes to acidic and alkaline conditions in anode and cathode, respectively. All the EKR experiments showed significant differences ($p<0.05$) when comparing with soil initial pH, with the exception of:

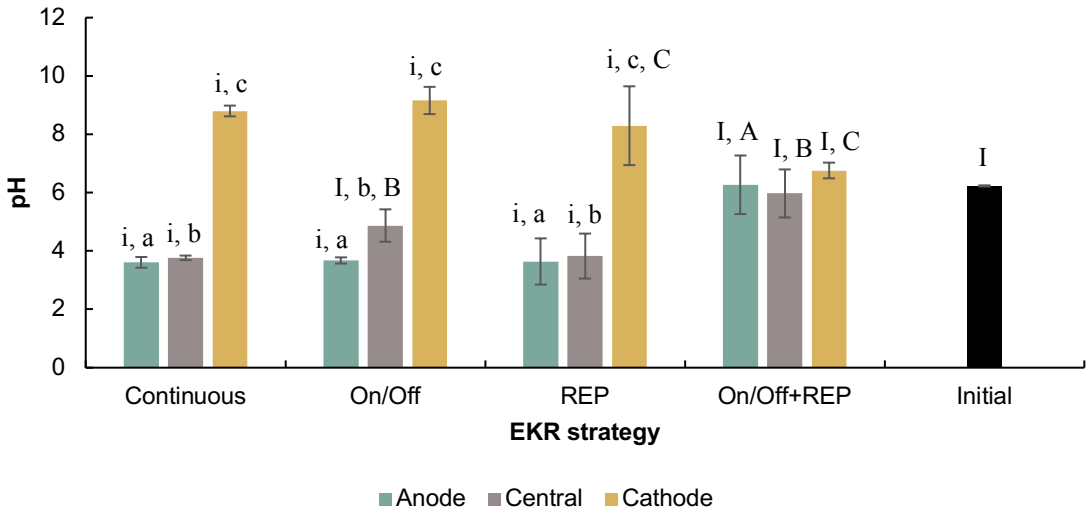
i) soil in the central compartment (pH= 4.9 ± 0.6; p>0.05) when the current was switched Off for 1 day (On/Off experiment);

ii) all soil sections (central, anode and cathode) in the On/Off + REP system.

When current strategies were applied, the greatly control of pH without the assistance of buffer solutions consisted in the change of electrodes polarity. These results show that switching Off the current for 24h does not significantly (p<0.05) affect pH changes comparing to a continuous current application (CC). In both cases, anode and cathode soil pH changed to acidic and alkaline, respectively, being statistically different from initial soil pH (p<0.05). The electro-polarization reversion for 24h, did not present significant advantages on maintaining soil pH, with all soil sections being different from the initial value (p<0.05). However, when combined the On/Off for 24h followed by REP for a longer period of time, 72h, pH remained somewhat similar between soil sections (anode, central and cathode; between (6.0 and 6.8), although still different from soil initial pH (p<0.05)

The acidification of the soil in the central compartment is expected when REP is not applied, being attribute to the effective ionic mobility of H^+ that is about 1.8 times higher that of OH^- and, under an electric field, the acid generated at the anode advances across the soil column, neutralizing the base (Acar, Y. B., & Alshawabkeh, 1993). The soil under study presented a low carbonate content, which according with the literature is related with low buffer capacity, not being able to effectively counteract the H^+ ions generated at the anode (Reddy et al., 1997). This was corroborated with the pH measurement after 24 h where the anode and cathode were already 2.9 and 10.3, respectively.

The effect of pH fronts is clearly observed under the application of continuous electric field. The gradient of soil pH in the direction anode-central-cathode might affect the mobility of pollutants in the soil.



Legend:
Statistical analysis: capital letters means NO statically differences (p<0.05):
I: significant statistical differences between initial soil pH and the different compartments for all the experiments
A: significant statistical differences for anode compartment between experiments
B: significant statistical differences for central compartment between experiments
C: significant statistical differences for cathode compartment between experiments

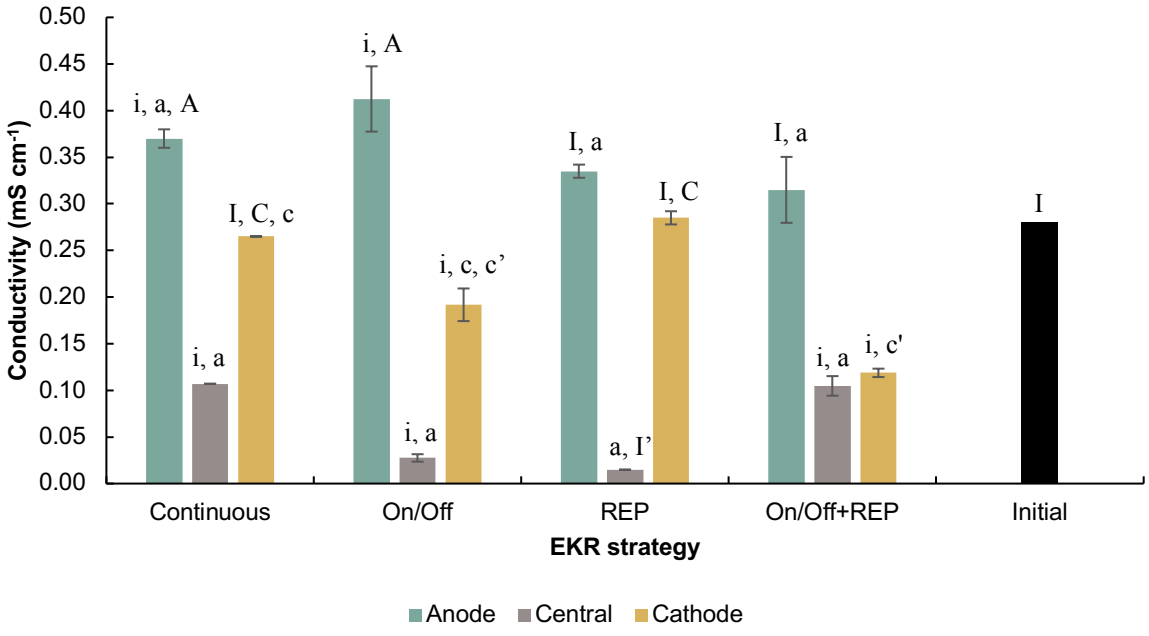
Figure 3.18 - pH values for the different EKR strategies applied in soil.

- *Conductivity*

Soil initial conductivity was 0.28 ± 0.0 mS cm^{-1} and 7 days after irrigating with spiked effluent it decreased to 0.19 ± 0.02 mS cm^{-1} (without DC; Figure 3.19). Comparing with the initial value, the conductivity decreased around ten times (p<0.05) in the central compartment for all the experiments. This decrease is attributed to ions migration, imposed by the electric field, from the central to the electrodes soil sections. No differences (p>0.05) were found between the central compartment of the distinct EKR experiments.

Between anode and cathode, all the experiments (except On/Off + REP) showed significant differences (p<0.05) comparing with the initial value. In the On/Off + REP the production of ions were balanced by the electro-polarization reversion for longer periods (for each electrode section the electrode was anode for 48h and cathode for 72h.

In the anode section the conductivity increased (p<0.05) for CC and On/Off experiments due to hydroxide ions generation. When the DC field was switched Off for 24 h (On/off and On/Off+REP experiments) a conductivity decrease in the cathode section was observed (p<0.05.).



Legend:
Statistical analysis: capital letters means NO statically differences (p<0.05):
I: significant statistical differences between initial soil pH and the different compartments for all the experiments
A: significant statistical differences for anode compartment between experiments
B: significant statistical differences for central compartment between experiments
C: significant statistical differences for cathode compartment between experiments

Figure 3.19 - Conductivity values for the different EKR strategies applied in soil.

- *Voltage*

The voltage dropped between the electrodes ranged from 3.3 ± 0.6 V to 27.6 ± 0.7 V. The voltage values had fluctuations along the time, in which high levels of voltage were registered.

The changes in the soil temperature were in the range of 23 ± 5 ºC not showing differences between compartments. The temperatures were also comparable for all the current strategies applied and are considered adequate and not affecting the performance of the biological activity (Esperanza Mena et al., 2016). Even though the soil temperature was kept constant, there was a slight moisture content decrease between daily irrigations (20 mL of deionized water was added daily). This small variations indicate water evaporation, which increase the electrical resistance (Page, M.M., Page, C.L., 2002) and, consequently, increased voltage drop. The water evaporation during EK can be a consequence of evaporation caused by room temperature during the day (kept at 22 ºC) and ohmic heating caused by the soil acting as an electrical resistor when an electric current is passed through it. The changes in soil moisture were visible mainly in anode side and are shown in Figure 3.20.

It is also important to mention that all the parameters previously mentioned are related with the electric current intensity and with higher current intensities higher soil changes can be expected (Risco et al., 2016).

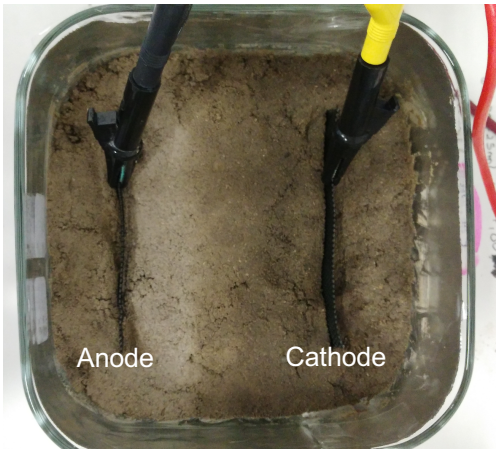


Figure 3.20 – Differences between of anode and cathode regarding soil water moisture.

3.4.2.2. EOC removal

In the present study the EOC selected were: SFM, CBMP, EE2, DCF, IBF and MBPh.

The amount of contaminants not detected in soil after EKR in relation to the initial amount determined in the soil after aging (spiking followed by 3 days at 6ºC) was considered as remediated.

- *Natural attenuation*

The influence of the current on EOC removal was observed through the EOC final presence in microcosms with and without electric current (control). The results presented in Table 3.11, showed that all EOC suffered natural attenuation in 6 days being the highest removal obtained for the antibiotic SFM (49±8%) followed by DCF ≈ IBF (46%) > EE2 ≈ MBPH ≈ CBMP (approx. 30%). EOC volatilization from soil is not expected due to the estimated Henry's Law constant of the contaminants in study. The photodegradation is not considered as the experiments were carried out indoor and the microcosms

were covered to avoid light at the substrate level. The influence of the indigenous microorganisms naturally presents in soil and, in this case, potentially introduced by irrigation with effluent, might justify the removals for the controls in 6 days.

The effect of soil sterilization showed to prolong the presence of EOC in soil, indicating that microbial activity played an important role in the degradation of these chemicals in soils (Xu et al., 2009). The biodegradation of EOC by microbial activity was already reported for several authors in soils and also in sediments e.g. (Conkle et al., 2012; Foolad et al., 2016; Lin and Gan, 2011; Thelusmond et al., 2018). Also, the irrigation with effluent also introduced nutrients, as phosphorus, particulate and dissolved organic matter (DOM) in soil. This might have impacts on the overall EOC remediation. (Annamalai et al., 2014) reported that EOC persistence decreased due to increased microbial activity, because DOM can serve as substrate for microorganisms. In the other hand, the dissolved matter from reclaimed water was also found to significantly increase the half-life of several EOC, while particulate matter was found to significantly decrease half-life of the same EOC (Dodgen and Zheng, 2016). Dissolved matter can (i) compete with EOC for binding sites in the soil matrix, reducing contaminants sorption and formation of non-extractable residues and can also (ii) bind with EOC and reduce their availability for microbial metabolism (Oh et al., 2016; Tolls, 2001; Zitnick et al., 2011).

- *Effect of the electric field*

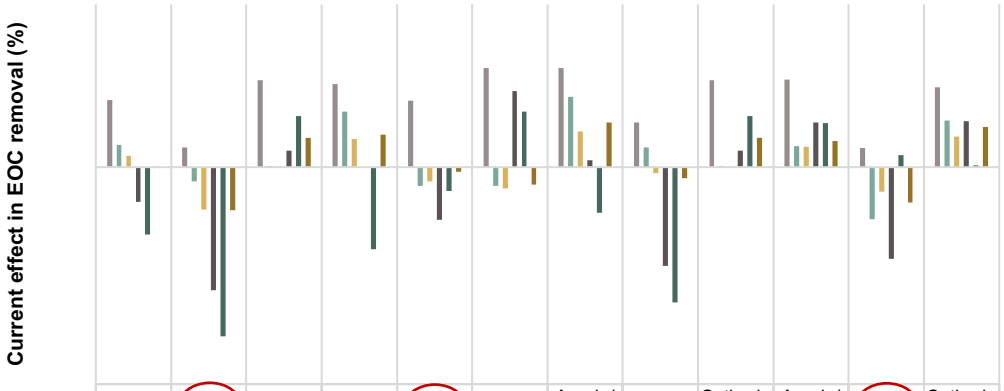
The Figure 3.21 shows that the DC electric current enhanced until 37% the compounds removal.

Among EOC, SFM was still the compound with better remediation efficiencies (up to 80%). Still, divergent degradation efficiencies were observed between the microcosm sections, with lower removals being observed in the central and a tendency of higher removals in cathode.

When CC was applied, EOC concentration in the central soil section reached values between 44 and 127% (SFM and IBF respectively) in relation to initial soil concentration (Table 3.11). DCF and IBF showed the highest concentration in central compartment. This fact might be an indication that EOC migrated towards the electrode. Similarly, to CC experiment, IBF also presented a concentration above 100% in the central soil section for REP (+14%; 3.14), with DCF concentration remaining around 100%.

Excluding SFM, the other EOC have 2.45 < Log K_{ow} < 4.5, which makes them easily adsorbed onto the soil organic matter than SFM (Log K_{ow} = 0.89). In terms of Log K_{ow} of the EOC follow the order: SFM (0.89) > CBMP (2.45) > BPA (3.32) > EE2 (3.67) > MBPh (3.82) > IBF (3.97) > DCF (4.51). There have been many attempts to correlate remediation with Kd and Log K_{ow} of compounds (Verlicchi and Zambello, 2015). Higher Log K_{ow} imply a higer Kd (solid liquid partition coefficient). This can justify the higher accumulation of IBF and DCF. These two compounds exist almost entirely in the ionized form at pH values of 5 to 9 (extremes depending on electrodes positioning), (pKa = 4.91 and 4.15, IBF and DCF). Being as an anion form they will migrate to the anode side. However, the pH changes in soil profile when approaching the anode side will make these compounds accumulating in central section as they are less mobile and strongly sorb to soil particles (Yu et al., 2013). The distribution of EOC

between aqueous and solid phase is dependent of sorption mechanisms, which in turn can also affect their degradation and mobilization during the ED process.



	Anode	Central	Cathode	Anode	Central	Cathode	Anode/ Cathode	Central	Cathode /Anode	Anode/ Cathode	Central	Cathode /Anode
	Continuous	Continuous	Continuous	On/Off	On/Off	On/Off	REP	REP	REP	On/Off + REP	On/Off + REP	On/Off + REP
SFM	25	7	32	31	25	37	37	16	32	32	7	29
CBMP	8	-5	0	20	-7	-7	26	7	0	8	-19	17
EE2	4	-16	0	10	-5	-8	13	-2	0	7	-9	11
DCF	-13	-45	6	0	-19	28	3	-36	6	17	-34	17
IBF	-25	-62	19	-30	-9	20	-17	-50	19	16	4	1
MBPh	0	-16	11	12	-2	-6	17	-4	11	10	-13	15

Figure 3.21 – Effect of electric current in the different sections of the microcosms (anode, central and cathode) in EOC removal from soil.

- *Current strategies*

Comparing all EKR strategies applied, the results show differences among the EOC removals (Table 3.11).

When the DC was switched Off for 24 h, the degradation in the central compartment improved with statistical differences (p<0.05) for DCF and IBF comparing with CC. Comparing the three soil sections in the On/Off system, the anode section presented lower concentration for CBMP, EE2 and MBPH, whereas the cathode had lower values of SFM, DCF, IBF (with statistical differences between anode and cathode for CBMP, (IBU; p<0.05). These differences can be justified with the fact that in cathode, IBF (pKa = 4.91) and DCF (4.15) have a pKa < pH of the soil in cathode. The same in central compartment when the current was switched Off. As these compounds are present in an ionizable form, solubility increase and electromigration towards the anode compartment increase. But when approaching the anode, the pH changes over the soil profile, makes IBF and DCF to preferential accumulate in central compartment. Contrary, CBMP, BPA, EE2 and MBPh have a higher pKa than soil pH, which make them more mobile to migrate by DC. Besides the pH control with On/Off, that showed to positively enhance IBF and DCF removal from soil compartment (Cameselle and Reddy, 2013) reported that the Off period during a continuous electric field gives time for the transfer from soil particles to soil moisture being then pulsed with switching On the current.

Regarding REP, a continuous current was maintained for over the 6 days, but the electrodes polarization shifted at day 3 for 24h. It is reported that REP favors the homogenization of the system as

it acts as a mixer by putting in contact pollutants, microorganisms and nutrients (Esperanza Mena et al., 2016). For REP the electroosmotic flow goes to both directions and an homogenous mobilization of EOC was expected for both directions. However, the limitation on EOC mobilization might be attributed to the unavoidable soil moisture changes during the day that limit the electroosmosis and diffusion transport processes of the EOC being considered as the key transport phenomenon for the removal of organic contaminants in soils, sludge and sediments (Cameselle and Reddy, 2012). The large number of variables that affect the electro-osmotic flow and their spatial and temporal variations under applied electric potential make it highly variable and very difficult to predict (Cameselle and Reddy, 2012). Besides the low moisture negatively affect the EK process due to the low soil conductivity, the soil moisture level is considered very important for the proper functioning of the biological process, as low soil moisture can also negatively affect the biological communities (Esperanza Mena et al., 2016).

By combining the On/Off + REP, removals remained similar to the other remediation strategies except for IBF in the central section (52±18% removal) with statistical differences comparing with CC and REP. The combination of periodic electric current with reversed electric polarizations seems to be a promising EK current strategy as it has potential to combine the advantages of both.

This study shows that once introduced in soil through effluent irrigation, 20%-100% of the studied EOC are present in the soil after 6 days of treatment, posing a potentially risk to the environment and human health. Some studies have already reported the presence of EOC in groundwater, which means that they can be mobile and leach through soil profile (Sui et al., 2015; Yu et al., 2013) due to the heavy rain and irrigation. (García-Santiago et al., 2017) highlight that special attention has to be paid to soil properties, since some persistent compounds with a high mobility in soil, like CBMP, may behave differently depending on soil texture and organic matter content. In some studies, CBMP was found to be accumulated in topsoil layers (Paz et al., 2016) and was rated as low according to its leaching potential (Oppel et al., 2004). Nevertheless, (Gielen et al., 2009) found that CBMP leached consistently below the top 0.9 m, while (Ternes et al., 2007) detected it in lysimeter effluents and groundwater samples from agricultural fields irrigated with treated wastewater for more than 45 years.

It should be pointed out that some samples had higher standard deviations (SD), which influence the statistical analysis and therefore, the comparison between current strategies and EOC removals. The high deviations obtained may be associated with EOCs compounds distribution along the two experimental duplicates as the microcosm were manually prepared by (i) putting 300 g of spiked soil in the cell and manual pressing to even the soil height along the microcosms and (ii) manual irrigation. Thus, it was accepted that there would be some variability in the results. Both factors may influence soil compaction and water distribution within the two different microcosms (n=2) which in turn may have influenced the EOC mobilizations/distribution in the soil column through electro-migration and -osmosis and diffusion. Also, no physical separation was used between soil sections, which may have led to a misdistribution when dividing the soil sections in the duplicate microcosms, thus influencing the SD.

Table 3.11 - Presence (%) of EOC after EKR (n=2).

Presence (%) of EOC													
		SFM		CBMP		EE2		DCF		IBF		MBPh	
EKR strategy		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Continuous (CC)	anode	26 ^{B}	14	69 ^{b}	11	67 ^{b}	11	77 $^{a, b}$	17	89 $^{a, b}$	16	70 ^{b}	8
	central	44 ^{B}	10	82 ^{b}	2	87 ^{b}	5	**110** $^{A, b}$	7	**127** $^{A, b}$	35	86 ^{b}	5
	cathode	19 ^{B}	7	77 ^{b}	5	71 ^{b}	4	58 ^{a}	5	45 ^{a}	9	60	2
On/Off	anode	20 ^{B}	7	57	15	61 ^{b}	11	64 ^{a}	12	94 $^{A, b}$	16	59	10
	central	26 ^{B}	19	84 ^{b}	23	76 ^{b}	12	84 $^{a, b}$	52	73 $^{A, a, b}$	47	72	17
	cathode	14 ^{B}	4	84 ^{b}	3	79 ^{b}	7	36 $^{a, B}$	9	44 ^{a}	12	77 ^{b}	6
REP	anode/cathode	14 ^{B}	5	51 ^{b}	4	58 ^{b}	0	62 ^{a}	3	81 $^{a. b}$	7	54	2
	Central	34 ^{B}	2	70	2	73	5	**101** $^{A. b}$	6	**114** $^{A. b}$	21	75	1
	cathode/anode	19 ^{B}	7	77 ^{b}	5	71^{b}	4	58 ^{a}	5	45 ^{a}	9	60	2
On/Off + REP	anode/cathode	19 ^{B}	17	69 ^{b}	4	63 ^{b}	8	48 ^{a}	26	48 ^{a}	18	61	3
	Central	44 ^{B}	19	96 ^{b}	6	80	9	98 $^{A, b}$	6	60 ^{a}	26	83	1
	cathode/anode	21	5	60	23	60	26	47 ^{a}	8	64 ^{a}	25	56	29
Control		51	8	77	6	71	4	64 ^{a}	4	64 ^{a}	2	71	1

Legend:
Red values mean the higher value among soil section (anode, central and cathode); The values in bold and red highlight the values higher than 100%;
The capital letter 'B' means statistical differences ($p<0.05$) comparing the contaminants presence for each treatment and each section (anode, central, cathode);
The capital letter 'A' means statistical differences ($p<0.05$) for each EOC in the different compartments between the EKR strategies;
Note: for SFM, CBMP, EE2 and MBPh statistical differences were not found for each compound among treatments in the different compartments (anode, central, cathode)

3.5. EOC removal from effluent

3.5.1. Simulated CWs

3.5.1.1. General results

The pH values for the W and WW assays are in Table 3.12. The pH significantly increased (p<0.05) either for the assays with water or effluent when LECA was present. The presence of LECA significantly increased the pH of the microcosms (p<0.05), mainly for the unplanted treatments (values from 8.3 to 10.7) when comparing with the 5.50 observed for the deionized water, control (W-C). The presence of plant did not significantly influence (p>0.05) the pH values. The increase of pH in the presence of LECA is attributed to its composition, that has alkaline components, such as oxides and carbonates that yield a pH-buffering capacity close to neutrality. The characterization of the material was studied by (Dordio et al., 2009, 2007) and the same pH pattern was found with a fast pH raise within the first 6 h to values close to 6, and after 3 days the pH of all the wastewaters tended towards almost neutral values in the 7–8.5 range, independently of their initial values in the 3 different types of wastewater. The pH of the influent is an important parameter because it controls several biotic processes, besides having a major influence in the occurrence of some important physico-chemical processes within the CWs (e.g., plant and microorganism development is favored by a neutral environment and the extent to which ionizable compounds are removed is frequently dependent on their degree of ionization which in turn is determined by the solution pH).

Table 3.12 - pH values for W and WW assays (mean ± SD, n= 2). Different letters represent statistically significant differences (p<0.05).

	CODE	3 days (W1)	7 days (W2)	7 days (WW1)	7 days (WW2)	14 days (WW2)
Treatments	L	10.5 ± 0.1 [a]	10.7 ± 0.3 [a]	9.6 ± 0.1 [a]	9.7 ± 0.2 [a]	9.9 ± 0.0 [a]
	P	-	6.0 ± 0.3 [b]	7.1 ± 0.1 [b]	7.1 ± 0.1 [b]	7.5 ± 0.2 [b]
	PL	-	9.8 ± 0.2 [a]	8.3 ± 0.2 [a]	8.5 ± 0.1 [a]	8.7 ± 0.2 [a]
Controls	W-C	5.5 ± 0.0 [b]	5.5 ± 0.0 [b]	-	-	-
	WW-C	-	-	7.4 ± 0.1 [b]	7.5 ± 0.1 [b]	7.9 ± 0.0 [b]
	$CV_{W/O\ LECA}$	-	5.6 ± 0.3 [b]	6.7 ± 0.2 [b]	7.1 ± 0.0 [b]	7.3 ± 0.0 [b]
	CV_{LECA}	-	8.8 ± 0.2 [a]	8.3 ± 0.1 [a]	8.2 ± 0.3 [a]	9.1 ± 0.0 [a]

Legend: W: assays in deionized water; WW: assays with wastewater (effluent) ; L: only with LECA; P: only with plant; PL: with both plant and LECA; W-C: Control with deionized water; WW-C: control in wastewater $CV_{w/o\ LECA}$: control (either with water or wastewater) vitality of the plant without presence of LECA; CV_{LECA}: control (either with water or wastewater) vitality of the plant with presence of LECA

The specie of plant *S. maritima* did not show visual signs of stress symptoms even when exposed to the higher EOC concentration. For the WW2 assay, the chlorophylls *a*, *b* and carotenoids contents were measured and the results are shown in Figure 3.22. No statistical differences (p>0.05) were observed between plants exposed (microcosms) or not exposed (controls vitality, without contaminants) to the EOC in the tested conditions.

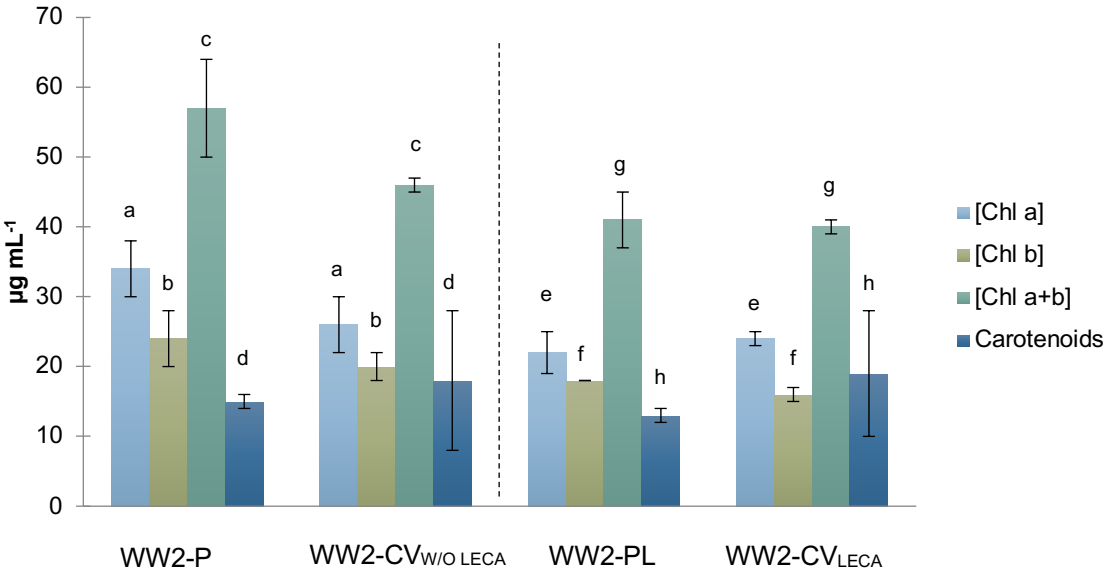


Figure 3.22 - Content of chlorophylls (a, b, total chlorophyll) and carotenoids (mean ± SD, n=2) at the end of the assay for S. maritima. Different letters indicate statistically significant differences (p<0.05) between treatments (WW2-P and WW2-PL) when compared to the CV (control vitality, without EOC).

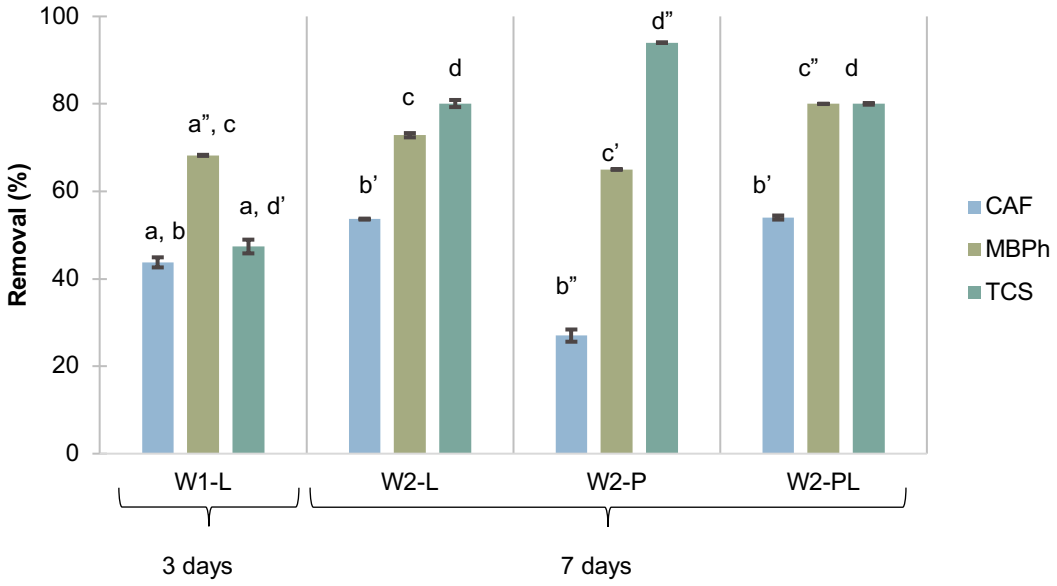
3.5.1.2. EOC removal

- *Simple aquatic media assays*

The experiments in a simple aquatic media (deionized water) allowed to assess the isolated role of LECA and the *S.maritima* in the microcosms. Figure 3.23 shows the removal efficiencies of EOC at the end of the W assays.

Considered the treatments only with LECA, higher residence time (7 days) increased contaminants removal in approx. 10-20% with statistical differences (p<0.05) for CAF and TCS. The influence of the contact time between contaminants and the support matrix was also reported in (Matamoros et al., 2015a). Even though the removals increase, the highest removal rate is achieved within the first 3 days.

The microcosms only with *S. maritima*, enhanced TCS removal in 13% with statistical differences comparing with the other treatments (removal of 94%; p<0.05) and without synergetic effects between LECA and plant in W2-PL. Also, for CAF and MBPh no synergetic effects between plant and LECA were registered showing similar removals (p>0.05) to the unplanted-beds (W2-L).



Legend:
a: statistic differences for W1-L treatment between CAF, MBPh and TCS;
b: statistic differences for CAF between the different variables (L, P and PL);
c: statistic differences for MBPh between the different variables (L, P and PL);
d: statistic differences for TCS between the different variables (L, P and PL);

Figure 3.23 - Rate of contaminants removed in simple aquatic media (W assays): after 3 days with LECA (W1-L) and after 7 days with unplanted LECA (W2-L), *S. maritima* (W2-P) and planted LECA (W2-PL) (mean ± SD, n=2). Different symbols (x, x', x") indicate statically differences (p<0.05).

- *Effluent assays (WW assays)*

Table 3.13 shows the removal efficiencies (%) for each contaminant at the end of assays with effluent (WW assays).

Comparing with the water assays previously analyzed, the removals of EOC in effluent were higher, therefore, the potential of LECA and plant promoting contaminants removal was less pronounced in effluent than in deionized water.

Comparing with control (only effluent and PPCPs), all the treatments: LECA (L), *S. maritima* (P) and planted LECA beds (PL) presented identical removals (p>0.05). The only exception was found for higher CAF removal by LECA (83%) than observed in the control (54%) and only in the presence of plant (44%). CAF has a very high solubility (2.16×104 mg L^{-1}) comparing to MBPh and TCS (60 and 10 mg L^{-1}, respectively), which justify the high removal (p<0.05) in WW1 when LECA was present comparing only with the presence of plant (WW1-P). The high removals by control for the three PPCPs can be explained by the possible presence of microbiological populations (Cydzik-Kwiatkowska and Zielińska, 2016), as the compounds in study have been reported as biodegradable (Gago-Ferrero et al., 2012; Matamoros et al., 2015, 2012; Zhang et al., 2013b).

In contrast with the WW1, the assay running in sequence (7 + 7 days, WW2) showed a lower CAF removal (54%; $p<0.05$) by unplanted LECA beds (L) when comparing with control (89%), whereas the presence of plant (P) and planted LECA beds (PL) provided a similar CAF removal (approx. 80%; $p>0.05$). For MBPh removals were around 97%; $p>0.05$ for all the treatments. After the second period of 7 days, there was a similar trend as the one observed for the first 7 days. Note that due to the high removal rate for TCS in WW1 experiment, this compound was not considered for the 7 + 7 days WW experiment.

In general, the results here presented suggest that LECA and *S. maritima* can be an option to consider for CWs as it showed capability to remove a high load of EOC in two cycles. The role of LECA in EOC removal was clear in deionized water assays, promoting 54%-80% of removal through sorption process, which are being largely dependent on the lipophilicity of the compounds (Luo et al., 2014). The higher removals of MBPh and TCS, compared to CAF, may be explained by their octanol water partition coefficient (Log K_{ow} > 3) and solubility, which promotes their retention by adsorption to the surface of the solid matrix. Even though the effect of LECA and plants was not so evident in PPCPs removal in effluent, some patterns can be drawn from the obtained results. It is believed that longer periods of time might lead to more pronounced differences. In the tested conditions, *S. maritima* showed a general tendency to promote higher removal of lipophilic than hidrophylic contaminants: TCS > MBPh > CAF. Phytoremediation processes that could contribute to the contaminants decrease are (i) uptake as recent studies increased the range of contaminants uptake (Carter et al., 2014; Wu et al., 2015; Zhang et al., 2013a), (ii) adsorption to plant roots, namely lipophilic contaminants and (iii) rhizoremediation as, e.g., the root can provide a surface area for attached microbial growth (Hijosa-Valsero et al., 2011). (Dordio and Carvalho, 2013) reported better performances obtained with planted systems in comparison with unplanted ones and to the important role attributed to the micro-aerobic zones produced in the rhyzosphere as well as adsorption to the roots and phenol uptake by the plants.

Table 3.13 - Removal efficiencies (%) for CAF, MBPh and TCS at the end of the WW1 and WW2 (mean ± SD, n=2). Upper and lowercase (x, X, X') letters represent statistically significant differences (p<0.05).

	Control (C)			**LECA** (L)			**Plant** (P)			**Planted LECA** (PL)		
	WW1	**WW2**		**WW1**	**WW2**		**WW1**	**WW2**		**WW1**	**WW2**	
	7 days	1st cycle (7 days)	2nd cycle (7 days)	7 days	1st cycle (7 days)	2nd cycle (7 days)	7 days	1st cycle (7 days)	2nd cycle (7 days)	7 days	1st cycle (7 days)	2nd cycle (7 days)
CAF	54 ± 10 a, C	89 ± 3 d, e, g	79 ± 4 d, e	83 ± 1 A, c	54 ± 0 D, e, g	65± 6 d, E	44 ± 6 a, C'	83 ± 0 d, e, g	84 ± 1 d, e	77 ± 1 A, C'	81 ± 2 d, e, g	85± 3 d, e
MBPh	61 ± 11 b, C	85 ± 2 e, G	89 ± 1 e	58± 1 b, C	97 ± 1 e, G	91 ± 0 e	64 ± 3 b, C	96 ± 0 e, G	> 97 e	65 ± 6 b, C	97 ± 0 e, G	> 97 e
TCS	85 ± 7 c, f	-	-	88 ± 5 c, f	-	-	93 ± 1 c, f	-	-	91 ± 2 c	-	-

Legend:
WW1 run for 7 days [treatments were spiked every 2 days making the concentrations range from 0.2 to 0.8 mg]
WW2 run for 14 days [treatments were spiked every 3 days (days 0, 3, 6 (1st cycle) 7, 10 and 13 (2nd cycle)) making the concentrations range from 0.1 to 0.3 mg]

Statistics: percentage statistically significantly different at p<0.05 comparing to:
a - CAF: WW1-PL with other WW1 treatments
b - MBPh: WW1-L with other WW1 treatments
c - between contaminants (CAF, MBPh and TCS) for WW1
d - CAF: WW2-L with other WW2 treatments
e - between 1st cycle and 2nd cycle in WW2 for each contaminant (CAF and MBPh)
f - TCS: WW1 between the different treatments
g - between contaminants (CAF, MBPh and TCS) for WW2 (first cycle, 7 days)

3.5.2. Electrodialytic process

3.5.2.1. General results

The effluent characteristics used in the present study are presented in Table 3.14 and is possible to see that "Eff2" sample had higher COD, BOD_5, TSS than the "Eff1", but Eff1 had twice higher P content. This result shows the variability of the effluent even though the samples were taken in the same month. The controls (without applied current) were performed with Eff1 and the ED experiments with Eff2.

Table 3.14 - Effluent characteristics used in ED experiments with effluent.

Effluent Code (Eff#)	TSS (mg L^{-1})	pH	Conductivity (mS cm^{-1})	BOD_5 (mg L^{-1})	COD (mg L^{-1})	P_{total} (mg L^{-1})
Eff1	17	7.31	0.95	6.1	47	11.5
Eff2	30	8.00	1.88	30	150	5.8

The pH and conductivity after the ED process and voltage drop are summarized in Table 3.15.

For controls (without applied current), there was no changes in pH and conductivity for both electrolyte or effluent.

For ED experiments, there was a pH decrease in anode due to the formation of H^+ ions, and a pH increase in the cathode compartment, due to the formation of OH^- ions. However, depending on the used membrane, the pH decrease, or increase was more pronounced i.e. when placed in anode or cathode and using the AEM or CEM, respectively.

The conductivity of effluent and electrolyte increased from the beginning to the end of the experiments. For A.AEM, the generation of H+ ions at the anode and the migration of the OH^- and NO_3^- from the cathode to the anode, as they can pass through the AEM increased the effluent conductivity by three times. Contrary, when a CEM was used with the effluent in the anode compartment (A.CEM) it only allowed the migration of cations out of anode, towards the cathode, thus the conductivity was lower at the end of the experiments comparing to the A.AEM (approx. less 55%).

The voltage drop behavior is in accordance with the changes observed in the conductivity. A slight variation of voltage between working electrodes was observed in all the cases. According to Ohm's law, to a fixed current, only a difference in the resistance could make the voltage change. If the voltage decreased, it means that the resistance also decreased. The degradation of EOC in effluent and/or electrolyte may cause the presence of more ions in solution and consequently increasing the conductivity thus decreasing the medium resistance.

Table 3.15 – The final pH, conductivity after ED treatment and voltage drop for the 2C-cell ED experiments with effluent.

	pH		Conductivity (mS cm^{-1})		Voltage (V)	
	Effluent	Electrolyte	Effluent	Electrolyte	Initial	Final
A.AEM	1.49	11.80	3.50	2.10	7.8	5.7
A.CEM	1.81	10.95	1.68	1.55	8.4	7.7
C.AEM	9.79	1.70	1.24	2.30	9.8	8.9
C.CEM	11.80	1.54	1.70	3.20	7.9	5.9

Legend:
AEM: anion exchange membrane; CEM: cation exchange membrane;
A.AEM and A.CEM: effluent placed in anode compartment using anion and cation exchange membrane, respectively.
C.AEM and C.CEM: effluent placed in cathode compartment using anion and cation exchange membrane, respectively.

3.5.2.2. EOC removal

In this study CAF, BPA, E2, EE2 and MBPh were the EOC selected to study the four set-ups of 2-compartments electrodialytic cells and the removals (%) are in Table 3.16.

At the end of the experiments the electrolyte was analyzed and none of the compounds were detected, which means that the removal was mainly due to electro-degradation instead of mobilization. However, the hypothesis of migration/mobilization and being degraded on electrolyte cannot be discarded because only the final electrolyte was analyzed and not during the experiment.

Regarding to the controls (without applied current), less than 20% of EOC removal was detected. Compound volatilization from effluent is not expected to be an important fate process based upon the estimated Henry's Law constant of the compounds here studied (> 10^{-4}). As the experiments were carried out in dark conditions, photodegradation is not a mechanism to consider. Therefore, these removals were attributed to biotic factors as the effluent was collected after the secondary settling tank, which is the treatment after the biological reactor and prior UV disinfection step, and some microorganisms might still be present. Also, superficial adsorption of EOC to the membranes may have happened. The voltage increase due to fouling was not observed during the 12 h of ED experiments, a slightly yellow color in AEM at the end of the experiments was observed, suggesting the adsorption of organic matter. In this sense, the presence of dissolved organic matter (humic substances) in the AEM may have promoted contaminants adsorption to the membrane, thus contributing to the high removals of contaminants with Log K_{ow} > 3 achieved in the C.AEM experiment. The CAF has a low Log K_{ow} (-0.07) and the highest solubility (2.16 × 104 mg L^{-1}) not being expected to adsorb into the AEM/ organic matter.

The removal order for the four set-ups in study was (excluding CAF): A.AEM ≈ C.AEM > A.CEM > C.CEM. This suggests that place where effluent is placed and membrane position influence the removals.

In the A.AEM and C.AEM, the removal values were, respectively, between 66–72% and 60–72% for BPA, E2, EE2 and MBPh, whereas in the A.CEM removals were between 30–63%. In general, CAF showed to be less susceptible to suffer electrodegradation not being removed when the effluent was placed in the cathode compartment (C.AEM and C.CEM).

The lowest removals were achieved in the C.CEM, between 8–36% also for BPA, E2, EE2 and MBPh. The presence of the CEM when effluent was placed in cathode (C.CEM) acted as a barrier as the anions cannot electromigrate to the anode compartment, after suffering deprotonation in the cathode. When placed in cathode, the pH of the effluent increased to values above compounds pKa, except for CAF (pKa=14), which is present as neutral. This means that BPA, E2, EE2 and MBPh suffered deprotonation, being present as anions, being thus able to electromigrate to the anode compartment through the AEM in C.AEM set-up. In cathode only indirect degradation can happen whereas in anode compartment contaminants will suffer both direct and indirect degradation (Klavarioti et al., 2009). Also, the pH in the anode compartment is acidic in which the hydroxyl radical has a standard reduction potential of 2.7 V whereas at alkaline pH it decreases to 1.8 V.

Table 3.16 - EOC removals (%) by ED process testing four 2C-cell designs.

Cell set-up	Removal (%) of EOC				
	CAF	BPA	E2	EE2	MBPh
A.AEM	**57**	**67**	**66**	**71**	**72**
A.CEM	30	39	38	49	63
C.AEM	1	**70**	**60**	**61**	**62**
C.CEM	0	8	15	14	38

Legend:
Bold values mean the highest removal for each EOC.
AEM: anion exchange membrane; CEM: cation exchange membrane.
A.AEM and A.CEM: effluent placed in anode compartment using anion and cation exchange membrane, respectively.
C.AEM and C.CEM: effluent placed in cathode compartment using anion and cation exchange membrane, respectively.
CAF: caffeine, BPA: bisphenol A; E2: estradiol; EE2: ethinyl estradiol; MBPh: oxybenzone)

3.5.2.3. EOC kinetics

The removal kinetic along the 12 h of experiment allowed to analyze the removal behavior of the compounds. The Figure 3.25 shows the normalized concentration as a function of time over the 12h. According with experimental data, the EOCs removal follow a pseudo first-order kinetics with correlations, R^2, higher than 0.9 and the corresponding law rate can be written as follows: $Ln(C/C0) = -kt$, where k is the reaction apparent rate constant (Table 3.17).

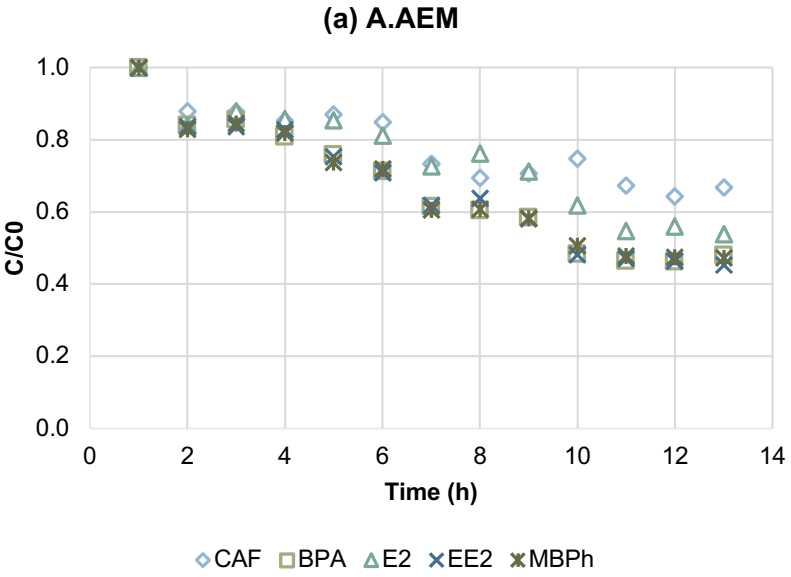
The highest removal rate constant was achieved in C.CEM for BPA (9.22×10^{-2} h^{-1}) with a correlation of 0.9888 and the lowest was in C.CEM for E2 (0.83×10^{-2} h^{-1}) with a low correlation (0.4061). EE2 in C.CEM also presents a lower correlation (0.7422). The obtained kinetics showed that the contaminants start to be removed immediately after the application of the electric current with pH changes in both cell compartments (20% decrease in the anode and increase in the cathode). (De Amorim et al., 2013) related the influence of pH in degradation kinetics e.g. the electrolysis carried out at different pH

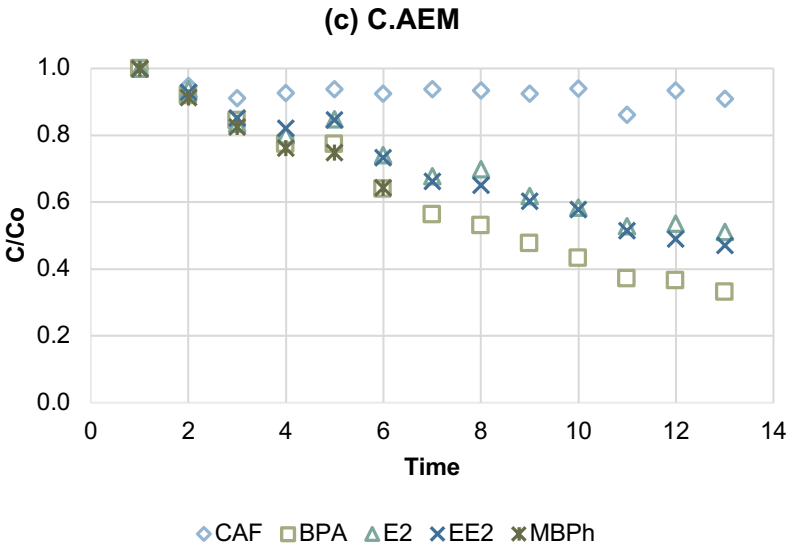
conditions pointed out that the degradation kinetics of both antibiotics were favored at acidic conditions. The effect of initial pH solution in BPA degradation had a pronounced effect with the rate constant (k) increase with the initial solution pH drop from 7.3 to 5.5, 4.0 and 3.0 (Yuan et al., 2013a).

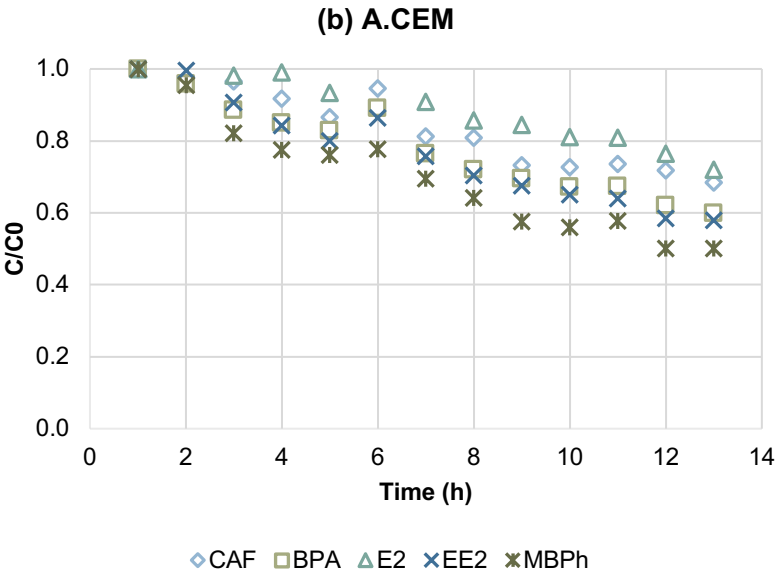
Table 3.17 - Pseudo first-order kinetics ($\ln$ (C0/C) = $-kt$) of EOC removal through (k x10-2 h-1).

Compound	A.AEM		A.CEM		C.AEM		C.CEM	
	k	R^2	k	R^2	k	R^2	k	R^2
CAF	3.96	0.8369	3.17	0.9205	*	*	*	*
BPA	7.12	0.9509	4.28	0.9545	9.22	0.9888	1.22	0.8233
E2	5.13	0.9147	2.27	0.8886	5.85	0.9674	0.83[a]	0.4062 [a]
EE2	7.15	0.9604	4.67	0.9665	6.32	0.9843	1.12 [a]	0.7422 [a]
MBPh	7.00	0.9541	6.12	0.9593	8.21	0.9926	2.40	0.9214

Legend: * no removal was observed; a: low correlation <0.8


(a) A.AEM
C/C0
Time (h)
CAF
BPA
E2
EE2
MBPh


(c) C.AEM
C/Co
Time
CAF
BPA
E2
EE2
MBPh


(b) A.CEM
C/C0
Time (h)
CAF
BPA
E2
EE2
MBPh

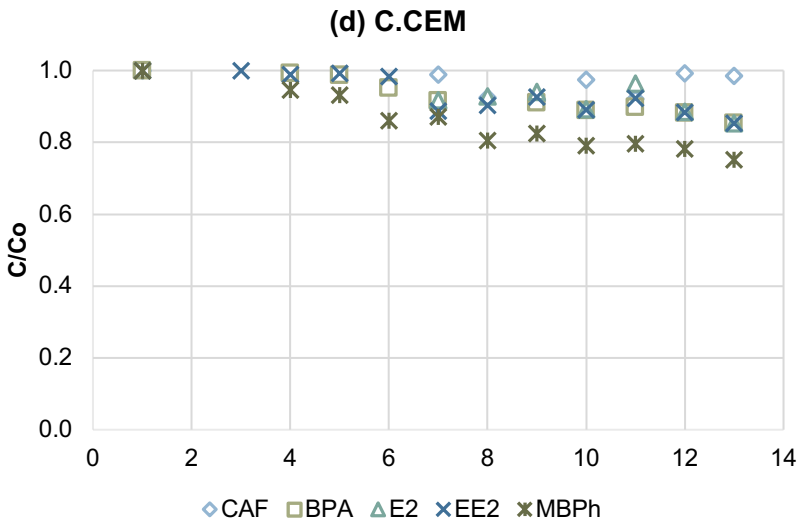


Figure 3.24 - Normalized EOCs concentration along the ED experiments.

3.5.2.4. Phosphorus recovery/reuse

Due to economic value of P and its utilization in agriculture as fertilizer, P should remain in the effluent for irrigation purposes, if the agricultural soil has lack of this nutrient. But, if the aim is to discharge the effluent, P concentration needs to be < 2 mg L^{-1} according to the Portuguese law, DL 348/98, November 9th. In order to achieve this target, P should be in cathode or anode compartment depending on the effluent final destination.

The percentage of phosphorus found in the anode or cathode end was calculated based on the initial P present in the effluent and it can be seen in Table 3.18. In all experiments, P mostly remained in the effluent after 12h of the ED process application meaning that more time or current, besides cell configuration, needs to be applied, if the goal is effluent discharge in aquatic bodies.

Table 3.18 - Amount of phosphorus (%) present in electrolyte after ED process.

Sample	Electrolyte P (%)
A.AEM	0.4
A.CEM	0.3
C.AEM	14.4
C.CEM	1.8

Legend:
Green color represents the best set-up for effluent use in agriculture;
Blue color represents the best set-up for effluent discharge in aquatic bodies.

Phosphoric acid molecule (H_3PO_4) can dissociate into three different species ($H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}), which correspond to the acidity constants (pKa, at 298 K) 2.12, 7.2, and 12, respectively. When the effluent is placed in the anode compartment, P remains in the effluent, because the acidic pH promotes neutral or monovalent phosphate forms (H_3PO_4/ $H_2PO_4^-$). In contrast, in the cathode compartment, the pH of the effluent becomes alkaline (>8), where phosphates are mostly present in their divalent and trivalent anionic forms (HPO_4^{2-}/PO_4^{3-}), which facilitates their electromigration towards the anode compartment. With effluent in cathode compartment and using AEM (C.AEM), 14.4% of total P electromigrated to the anolyte, contrary of what happened when a CEM was used (C.CEM), as this membrane hinders the electro-migration of negatively charged phosphates.

Having in mind the reuse of effluent in agriculture, the best cell design seems to be A.AEM as high EOCs removal were also achieved. If the aim is to discharge the effluent to the receiving waters, a low P content is required, and the best option seems to be C.AEM.

3.5.2.5. Final set-up

The final set-up is shown in Figure 3.25 and consist in an ED cylindrical reactor with an AEM with polarization control switch. This system allows the WWTP operators to define the polarization of the effluent compartment according to effluent final desired use:

(A) discharge the effluent to receiving waters – cathode, so remaining P is recovered in the electrolyte (anode end, through electro-migration);

(B) agricultural irrigation – anode, so that phosphorus remains in the effluent, thus producing a fertilizer solution; Moreover, an important advantage for the WWTP is the simultaneous EOC removal and nutrient (in this case P) recovery.

Still, in both cases, further optimization of ED parameters is needed to improve simultaneous EOCs degradation and P migration to the anolyte (electrolyte). Further studies with this set-up should be carried out with higher current intensity and short periods of time. The EOC removal will potentially increase as well as the amount of P recovered. Besides the technical feasibility, the economic feasibility needs to be also considered for any technology to be suitable for use in the industry. Major expected costs associated with the effluent treatment by ED process are in the electricity and membrane that might need to be changed/washed periodically. Considering an energy price of 0.15 € kWh^{-1} the energy costs were calculated through the following equation:

$$\boldsymbol{Energy\ consumption}\ (\boldsymbol{kWh}) = \frac{\boldsymbol{V}\times\boldsymbol{A}\times\boldsymbol{h}}{\boldsymbol{1000}}$$

V = cell voltage average, Volts
A = applied current, Amps
h = time of treatment, hours

The costs of the treated effluent ranged between 1.1 and 1.8 € m^{-3}. Comparing to other treatments, also based on compounds oxidation, namely advanced oxidation process (AOPs), the associated costs are in a range of 21.0 € m^{-3} for UV/US/O_3 to 3 660.5 € m^{-3} for US alone, 5.90 € m^{-3} to 21.4 € m^{-3} for US + UV treatment and US alone, respectively and 15.3 € m^{-3} for US + UV + H_2O_2 to 3 346.4 € m^{-3} for US alone. Also considering only the energy costs (Mahamuni NN, 2010) this shows that ED process is a competitive technology to be implemented in a WWTP as a effluent polishing step avoiding the environment contamination and the risks for the human health through the discharge if EOCs contaminated effluent.

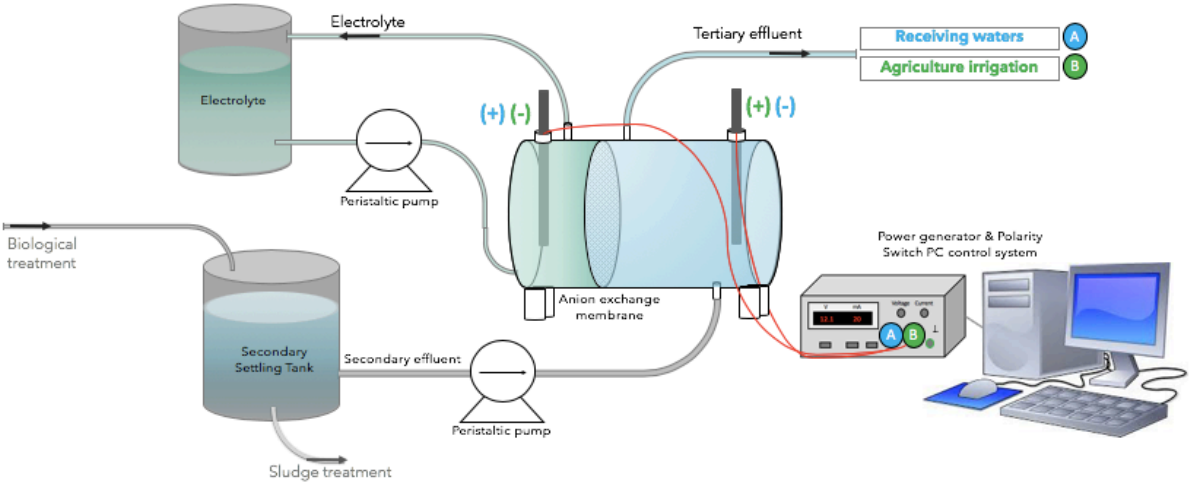


Figure 3.25 - Electrodialytic effluent treatment apparatus in which polarity is defined according to effluent desired final use A) receiving waters (catholyte and effluent in anode end); B) Agricultural use (anolyte with effluent in cathode compartment).

3.5.3. Electrokinetic reactor in a vertical flow mode

3.5.3.1. General results

In the present work SFM, CBMP, BPA, EE2, DCF and MBPh were the six EOC selected as a model for these experiments.

The present investigation was undertaken to extend the knowledge about the electro-degradation of EOC in a continuous flow mode. The electrode material and current density are two important parameters on contaminants removal in electrochemical process and the suitability for EOC removal from effluent was here studied.

The initial effluent sample presented an alkaline pH (8.56) and the parameters were within the Portuguese legal limits for discharge into water bodies (DL 236/98) (values not show). An initial screening of the studied contaminants was carried out in the effluent used, and all were below the analytical detection limits. The initial and final pH and conductivity values, as well as the voltage drop of the experiments are shown in Table 3.19. The effluent had an alkaline pH (8.56) and 1.82 mS cm^{-1} of conductivity. The pH of the effluent had the tendency to decreased, mainly for higher current intensities and when graphite anode was used. The conductivity slightly decreased for the lowest current intensity and remain similar for the highest due to the greater production of ions in electrode. The presence of Cl^- and other inorganic ions in the effluent yielded sufficient conductivity for the direct EK treatment without adding any salt as supporting electrolyte.

In both cases, using graphite or Pt/Ti as anode, the voltage had slightly variations over the experiment, mainly when high current intensities were applied.

Table 3.19 – pH, conductivity and voltage drop for EK reactor with continuous effluent flow mode.

Current intensity (mA)	Electrode material		pH		Conductivity (mS cm^{-1})		Voltage (V)	
	Anode	Cathode	Initial	Final	Initial	Final	Initial	Final
25	Graphite	Pt/Ti	8.56	8.11	1.82	1.72	7.2	7.0
	Pt/Ti	Pt/Ti	8.56	8.51	1.82	1.63	6.9	7.0
100	Graphite	Pt/Ti	8.56	7.25	1.82	1.85	14.8	16.7
	Pt/Ti	Pt/Ti	8.56	7.46	1.82	1.85	14.8	16.4

3.5.3.2. EOC removal

Table 3.20 shows the presence of EOC after EK treatment with a low current intensity (25 mA) and increasing 4 times the intensity of the current (100 mA).

- *Differences between the tested electrodes*

Between the two anodes, Pt/Ti and graphite, no significant differences were found in terms of EOC removals including for both intensities. The electrochemical method only uses the electron as the main reagent for contaminants removal being the generation of $OH^{\cdot}$ from the water oxidation at anode crucial for EOC removal. The Pt/Ti and graphite anode electrodes are both considered active electrodes (Rivera-Utrilla et al., 2013), and the electrogenerated hydroxyl radicals are expected to be converted in “adsorbed oxygen”, which is consumed in the oxidation of organic compounds with the formation of selective oxidation products and in an easy oxygen evolution (Scialdone et al., 2011). Even though in the tested conditions no differences were found between the two anodes, (Sifuna et al., 2016) reported that Pt electrode is greater than graphite in SFM and DCF removal. The authors attributed the differences with the different adsorptions of hydroxyl radicals on these electrodes: due to Pt the hydroxyl radicals are weakly adsorbed and have a lower enthalpy of adsorption on the Pt surface. Consequently, they are very reactive and effective towards oxidation due to the faster reactions with all organics arriving at the surface and in the vicinity of the anode. On the other hand, carbon electrode has more hydroxyl radical strongly adsorbed on its surface; thus it is less reactive toward contaminants (Sifuna et al., 2016). In addition, higher current intensities can lead to more energy dissipation and shorten the life of electrode (Niu et al., 2016). In the end of the experiment, the graphite electrode showed signs of corrosion due to the effect of the applied current (Figure 3.26). Higher current could lead a part of electric energy transfer to thermal energy and result in a larger invalid consumption of the giving charge. Even though high current intensity caused electrode material corrosion, side reactions including oxygen

evolution could also happen at the same time and no differences between the two electrodes in terms of EOC removal was registered for the tested conditions (Marselli et al., 2003).

- *Current intensity effect*

Comparing with controls (without applied current) the effect of the lowest current applied (25 mA) promoted 10% to 70% of EOC removal, with CBMP not being removed and MBPH with the highest removal. When increasing the current density by 4 times (100 mA) the removals increased 10-30%. The increase of the current intensity promotes the generation of more OH, which is responsible for the organic removal, and hence, more removal of EOC was expected.

The effect of the current can also be related with the continuous flow mode present in this work, which according with (Scialdone et al., 2011) are strongly interrelated and must be considered together. A continuous flow mode influenced the contact between electrode surface and effluent, which is shorter than operating in batch mode. In the vertical EK flow reactor the effluent was in a continuous flow mode passing first through Pt/Ti cathode electrode where reduction reactions take place going towards anode where hydroxyl radicals are formed. The oxidation of the organic by hydroxyl radicals generated from the water oxidation is so fast that the rate determining step is the mass transport from the bulk solution to the anodic surface. When the rate of the mass transfer of the organic to the anodic surface is dramatically lower than the rate of oxidation, the concentration of the pollutant at the anodic surface/reaction layer is close to zero and the oxidation process is under mass transfer control (Scialdone et al., 2011).

Regarding the differences among the contaminants for the two tested current intensities, MBPh showed the highest removal rate (83%) with CBMP and also DCF with the lowest removals, showing a slight difference comparing with control. The molecular structures of the compounds have a strong influence in the success of electro-chemical removal. Compounds characterized by the presence of electrophilic halogen groups with a negative inductive effect at the aromatic ring as BPA or by the absence of nucleophilic substituents with an activating effect on the aromatic ring as DCF and IBF (not present in this study), are more recalcitrant because they decrease the reactivity toward oxidant agents ($^{\bullet}OH$) and active chlorine species present in effluent (Garcia-Segura et al., 2015)

The EOC required significantly longer electrolysis time to be effectively oxidized. The results from this study show that the electrochemical degradation is a promising method for EOC removal, but operational parameters need to be optimized. In the following section (*Section 3.5.4*) experiments in batch mode were carried out. Graphite electrode did not show to be resistant to the tested conditions (Figure 3.26), therefore was not considered in the coming experiments.

Table 3.20 – Presence (%) of EOC after EK vertical continuous flow reactor applying different current intensities and different anode materials.

Current intensity (mA)	Electrode	SFM	CBMP	BPA	EE2	DCF	MBPh
0 *		110 ± 0	77 ± 2	119 ± 6	106 ± 7	108 ± 4	94 ± 9
25	**Graphite**	91	72	98	65	93	21
	Pt/Ti	93	71	94	71	98	19
100	**Graphite**	64	61	89	56	79	11
	Pt/Ti	60	**60**	**85**	56	**73**	11

Legend:
*the control was carried out without applied current

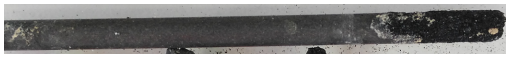


Figure 3.26 - Graphite electrode with signs of corrosion after EKR.

3.5.4. EK reactor working in batch mode

3.5.4.1. General results

The final pH, conductivity and voltage values of the experiments are in Table 3.21.

Initial effluent samples pH was 7.99 ± 0.15. After EK, pH slightly increased in the range of 0.12 as minimum and 0.9 maximum. The small changes in pH were expected because electric current was applied and the •OH generated by the catalytic electrode can form hydroxide ions, which might result in a pH increase (Tung et al., 2013). Also, the slightly changes in effluent pH could be due to the slow accumulation of carboxylic acids that are then oxidized by •OH in the mineralization process of EOC. This fact is reported in (Wang et al., 2016) where pH of the solution decreased slowly from 5.2 to about 4.3 at ~30 min and increased to 5.7 at ~60 min during electrolysis.

The effect of pH, mainly the initial pH, on anodic oxidation has been well reported in literature as it can influence oxidation mechanisms and surface properties of photocatalysts, leading to adverse effects such as aggregation of semiconductor particles, repulsion force between organic compounds and photocatalyst surface or lower production of hydroxyl radicals e.g. (An et al., 2012; Pérez-Estrada et al., 2005). On other hand, (Brillas et al., 2005a) showed that paracetamol can be completely removed with Pt electrode and its kinetics follows a pseudo-first-order reaction with a constant rate independent of pH. The findings are diverse and sometimes even contradictory, depending on the types of target pollutants, types of anodes and also types of electrolytes (Pérez-Estrada et al., 2005; Tung et al., 2013). It should be pointed out that the here tested EK technology does not need any addition of reagents to change the pH and has the advantage of maintaining effluent pH, being an asset if, e.g., effluent is reused for agriculture irrigation.

The conductivity was kept somewhat constant throughout the experiments. As conductivity express an estimate of the number of free charges in a solution, and if the ions produced at the electrodes do not result in higher conductivity, a constant conductivity indicates that the concentration of other ions were decreased. In all cases, the voltage tends to slowly decrease indicating decreasing resistance over time, further supporting this hypothesis. It should be noted that MMO material allowed a significant reduction of cell potentials (voltage values lower than Pt/Ti).

Table 3.21 - pH, conductivity and voltage of the experiments and the respective initial values.

EK experiment #	Anode material	Shape	pHi	pHf	Cond i (mS/cm)	Cond f (mS/cm)	Vi (V)	Vf (V)
1.1	MMO	bar	8.00	8.64	1.23	0.88	26.4	26.3
1.2	MMO	bar	8.00	8.56	1.23	1.09	26.4	26.2
1.3	MMO	bar	8.01	8.51	1.10	1.20	29.7	26.2
1.4	MMO	bar	8.29	8.47	1.45	1.40	23.2	21.0
2.1	Pt/Ti	bar	8.00	8.59	1.23	1.22	30.1	26.4
2.2	Pt/Ti	bar	8.00	8.6	1.23	1.22	30.4	26.5
2.3	Pt/Ti	bar	7.84	8.75	1.26	1.27	24.6	24.7
2.4	Pt/Ti	bar	8.29	8.53	1.45	1.38	24.5	24.1
3.1	Pt/Ti	Mesh	8.00	8.3	1.23	1.08	24.0	21.0
3.2	Pt/Ti	Mesh	8.00	8.12	1.23	1.15	23.9	21.4
3.3	Pt/Ti	Mesh	8.01	8.21	1.10	1.05	24.5	20.0
4.1	MMO	Mesh	7.91	8.28	1.10	1.02	20.2	19.6
4.2	MMO	Mesh	7.88	8.36	1.19	1.11	19.2	18.4
4.3	MMO	Mesh	8.01	8.42	1.15	1.29	22.9	19.0
4.4	MMO	Mesh	8.01	8.43	1.15	1.41	18.6	17.5
5.1	MMO	Circular	8.00	8.44	1.45	1.12	19.5	17.9
5.2	MMO	Circular	7.84	8.12	1.25	1.25	16.9	16.1
5.3	MMO	Circular	7.84	8.16	1.26	1.30	18.0	17.6
5.4	MMO	Circular	7.84	8.18	1.26	1.29	15.4	15.3

3.5.4.2. EOC removal

Differences among EOC removal were observed for the different electrode materials tested in the electrochemical reactor, ranked by increasing removal percentage:

- CAF and CBMP: 46±5% and 36±15%;
- BPA, IBF and MBPh: between 59%±5% and 78±9%;
- SFM and DCF: approx. 90%;
- E2 and EE2: higher than 90% (below LD; 0.2 ppm).

The presence of each EOC in the end of the experiments are in Table 3.22.

The differences between the EOC removals can be mainly attributed to their structure, which influences the electrochemical degradation. It has been reported that •OH generated from water electrolysis, play

a vital role in electrochemical oxidation mechanism of organic chemicals. A study with EE2 proved that •OH and radical chain reactions might be the main contribution for EE2 destruction in the electrochemical catalysis (Feng et al., 2010). In the present study, the analysis of effluent samples in GC–TOFMS revealed the presence of oxalic acid after EK treatment using MMO circular mesh as anode, which come from the destruction of the benzenic ring of aromatic pollutants by •OH (Brillas, 1998).

CAF and CBMP have a pKa higher than effluent pH (pKa of 14.0 and 13.9, respectively), which might influence degradation mechanisms. For electro-organics reactions one or two deprotonations must precede the electron transfer step with the electrode material (Carlesi Jara et al., 2007). CAF and CBMP have a very stable protonated group, the tertiary amine of the ring and when the solution pH is smaller than molecule pKa, deprotonation is more difficult. It is thus possible to deduce that deprotonation might be the rate controlling reaction step, similarly to the antibiotic lincomycin (Carlesi Jara et al., 2007), where the slow overall abatement was explained by an intrinsically slow primary electron transfer and by the fact that chemical reaction coupling has to take place.

The other EOC were in their ionized form (pKa < pH), which make them more soluble and probably more available to •OH attack. (Pérez-Estrada et al., 2005) reported the importance of the pH lower than the pKa for DCF, in order to avoid the precipitation of the compound thus influencing the removal.

Table 3.22 - Presence (%) of EOC at the end of the EK treatment for the five different anodes tested with a fixed MMO cathode bar.

Anode material	EOC presence (%)								
	CAF	**SFM**	**CBMP**	**BPA**	**E2**	**EE2**	**DCF**	**IBF**	**MBPh**
MMO bar	96 ± 4	53 ± 20	92 ± 10	70 ± 19	56 ± 25	58 ± 26	60 ± 13	104 ± 5	74 ± 13
Pt/Ti bar	**54** ± 5	25 ± 13	**64** ± 15	55 ± 28	56 ± 22	46 ± 18	11 ± 3	**41** ± 5	48 ± 25
Pt/Ti mesh	77 ± 1	62 ± 2	90 ± 3	65 ± 2	81 ± 5	87 ± 5	72 ± 2	89 ± 4	61 ± 2
MMO mesh	99 ± 14	60 ± 21	98 ± 8	71 ± 19	67 ± 15	72 ± 11	70 ± 15	114 ± 13	69 ± 21
MMO circular mesh	61 ± 10	**9** ± 9	76 ± 6	**30** ± 20	**<LOD**	**<LOD**	**10** ± 2	48 ± 2	**22** ± 9

Legend:
bold values mean the lowest presence for each EOC among the different EK experiment (MMO bar, Pt/Ti bar, Pt/Ti mesh; MMO mesh; MMO circular mesh)

It should be mentioned the variability of the effluent under study. As previously stated the experimental design took in consideration different sampling times and the differences on EOC removal between replicates of the same experiments might be correlated with the effluent characterization parameters.

The existence of relationships between the concentration of some pharmaceutical compounds and influent wastewater characterization parameters (e.g. COD and BOD) and between the removal of the pharmaceutical compounds and the removal of wastewater characterization parameters is reported by (Santos et al., 2009). Positive correlations between effluent characteristics and EOC removals could be

explained through the dissolved organic matter competition for the electrogenerated •OH, which is commonly characterized by BOD and COD values.

Furthermore, other chemically mediated reactions may also increase compounds degradation, for example, through reactions with Cl, that is usually present in the wastewater (Xue et al., 2011). Due to the fluctuation of the effluent quality in WWTP it is of practical interest to examine how the initial effluent sample, e.g. COD value affects the EOC removal from effluent in EK-based technologies.

Comparing the results from the previous Section *(3.5.3.2.)* with the Pt/Ti electrodes, the removals achieved in batch reactor are much higher. However, it should be noted that in the previous section the set-up refers to a system operated in continuous flow regime and, therefore, the differences to a batch assay, as is the case of this study, should be weighted in that comparison.

3.5.4.3. Electrodes performance

The five types of anodes performed considerably differently (p<0.05) in terms of EOC degradation (Table 3.22). The best result was obtained with MMO circular mesh followed by Pt/Ti anode bar, with MMO coupling good efficiencies with lower energy consumption. The other three electrodes had a similar performance in terms of EOC removal with MMO bar having the lowest removals (from 0% to 53%± 20%).

It is well accepted that the use of an anode material with a high oxygen evolution potential is desirable for organic oxidation because of its inhibition of power losses to oxygen generation (Li et al., 2005).

The differences among the electrodes can also be seen through the cyclic voltammetry and the chronopotentiometry. The MMO bar was used as counter electrode and saturated calomel electrode (SCE) as the reference electrode in 10^{-3} M $NaNO_3$ at scan rate of 100 mV s^{-1}.

The oxygen evolution potentials of the four working anodes were determined using cyclic voltammetry (**Error! Reference source not found.**). The anodic oxidation potential was very different following the anode material. The domain for Pt/Ti mesh and bar was at 1.2 and 1.5 V vs. Ag/AgCl, respectively. But for MMO where a steady increase of the current is observed the definition of the electroactivity domain was difficult.

According to the chrono potentiometry results (Figure 3.28), the MMO circular mesh anode has by far the highest anode working potential and the MMO bar the lowest working potential taking more time to reach the potential. The low anode potential of MMO bar is probably related with the low •OH generation during the EK process, and thus it demonstrated the lowest effectiveness for EOC degradation. The use of a circular mesh provided a higher surface area to volume ratio and thus, compared to the other anodes tested, greater potential for •OH production, and subsequently faster and stronger EOC degradation. This is supported by the results attained for the MMO circular mesh compared to the bar that presented lower removals between 53% ± 20 – 104% ± 5 (Table 3.22).

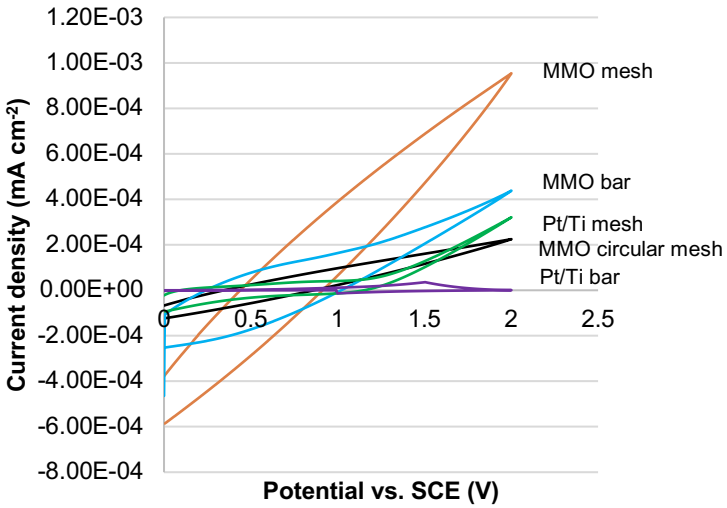
The exact catalytic role of the anode surface in organic oxidation is still under discussion. It is generally believed that organic compounds in aqueous solutions can be oxidized on an anode by direct electron

transfer and indirect oxygen atom transfer. In the direct electron transfer process, organics are adsorbed on the anode surface and give up electrons to the anode. With the indirect oxygen atom transfer, it is generally considered that oxygen radicals, especially the •OH generated from water electrolysis, play a critical role in the EOC oxidation mechanism of organic substances.

The direct anodic oxidation is attractive because it does not need chemical additives, which may cause secondary pollution. The main problem during direct anodic oxidation is the deactivation of the anode surface, due to the formation of polymer on the surface (Li et al., 2005). In the present work, the surface of the electrodes appeared to affect the EOC oxidation mechanisms, when comparing the Pt/Ti bar and mesh (Table 3.22). In terms of EOC oxidation, the Pt/Ti bar showed better performance than the mesh and similar to the MMO circular mesh. In addition to •OH generation, the electrodes surface might have a property that is favorable to the adsorption and direct oxidation organics. These electrodes could be somewhat less efficient in the adsorption of small organic molecules and in electron transfer from the organic to the anodes.

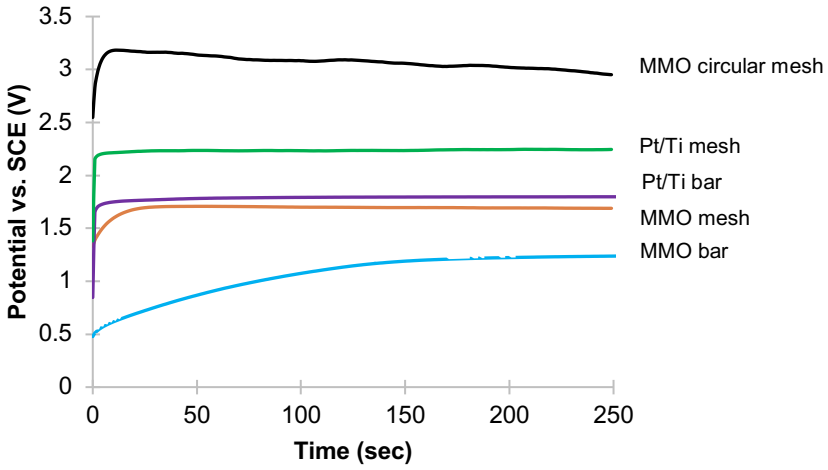
In the anodic oxidation process, active sites on the anode surface may participate in •OH production, whereas other sites function in the adsorption and activation of organic molecules. Therefore, the greater the number of active sites the higher is the catalytic ability of an anode (Cui et al., 2009). Organic species have the tendency to adsorb on the platinum electrode surface, as well as, by its easy generation of active oxygen species (Carlesi Jara et al., 2007). However, adsorption interactions between organic compounds and anode material and formation of a polymer layer on the anode surface can lead to the deactivation of the anode (poisoning effect) (Panizza and Cerisola, 2009). Thus, the oxidation signal disappears due to the possible formation of a polymeric film on the surface of the electrode. In organic wastewater treatment, anodic oxygen evolution actually causes a power loss, which reduces the overall current efficiency for both direct and indirect organic oxidation (Stucki et al., 1991). The use of an anode material with a high oxygen evolution potential is especially desirable since it can decrease the unwanted power loss to oxygen generation. The experimental results suggest that the different anode surfaces have different degrees of reactivity towards EOC degradation.

The generation of •OH from water electrolysis is largely responsible for the destruction of most organic chemicals during the EK process (Terashima et al., 2002). The difference in the effectiveness and performance of different anode materials for wastewater treatment demonstrates the complexity of the EOC reaction mechanisms involved. It is important to point that at the end of the experiments all the anode materials showed to be resistant to corrosion to the current applied.



SCE: saturated calomel electrode

Figure 3.27 - Electrochemical properties of the five different electrodes: cyclic voltammetry for the oxygen evolution potentials.



SCE: saturated calomel electrode

Figure 3.28 - Electrochemical properties of the five different electrodes: chrono potentiometry for the anodic potentials and the current density of 0.5 mA cm^{-2}.

3.5.4.4. Set-up optimization

- *Current effect*

The results regarding the experiments with different current intensities can be seen in Figure 3.29. Current intensity is considered an important operating parameter in electrochemical oxidation of organics at MMO anodes, for the purpose of both mechanistic study and cost-effectiveness analysis (Wu et al., 2014). It is reported that mineralization increases with current intensity (Brillas et al., 2005b). However, in literature is not linear that higher current intensity will be more efficient for all the processes.

In the present work, increasing the current intensity (125 *vs.* 175 mA) had a positive influence (without statistical differences; p>0.05) only for the compounds that already showed higher removals with 100 mA. On the other hand, CAF, CBMP and IBF had similar removals between the two current intensities tested and comparing with 100 mA. The increase of the current promote the direct anodic oxidation of pollutants, but also enhance the production of hydroxyl radicals (Brillas et al., 2005b; Tung et al., 2013). Therefore, efficiency drops since too high current density can increase the portion of current wasted due to the increase of secondary reactions (such as oxygen evolution at the anode and H_2 evolution at the cathode) (Panizza and Cerisola, 2009). This result indicates that current intensity did not influence the efficiency of the EOC remediation in the tested conditions, with MMO anode suggesting a significant role of mediated processes. In (Sopaj et al., 2015) the current density did not influence the efficiency of amoxicillin mineralization with DSA (Ti/RuO_2–IrO_2) anode electrode and the authors suggested a significant role of mediated processes.

In the present study the trends observed for MMO circular mesh electrode, clearly indicated that the process is more efficient working under lower current densities, showing typical behavior of a diffusion-controlled process in which, a higher current intensity leads to lower efficiencies due to the occurrence of wasting reactions. Hence from above suggestion, a current of 175 mA (splitting in two) with a submerged MMO circular mesh electrode with an area of 105.80 cm^2 was chosen for the proof-of-concept.

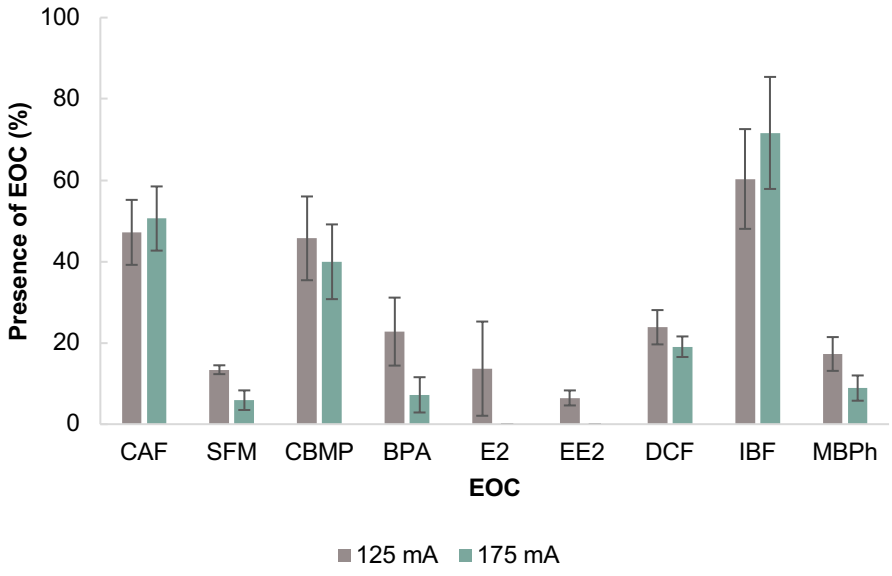


Figure 3.29 - Different current densities tested with the best anode material and shape for EOC removal previously tested (MMO circular mesh) (n=3).

- *Temperature effect in EKR*

It should be noted that since electrochemical oxidation is an exothermic process, heat can be generated. With the increase of the current intensity (175 mA), an increase of effluent temperature, approx. 4 ºC in 2 hours of experiment, was verified. Thus, “high” operating temperatures may be

maintained without the use of an external heating system when using high current intensities. To assess the possible temperature effect on EOC degradation, experiments (n=2) in deionized water and 2 mg L^{-1} of each EOC were carried out in a glass beaker with magnetic stirring to keep homogeneous conditions under room temperature 22 ºC and heated to 30 ºC. The results revealed no differences (p>0.05) between the two temperatures in terms of EOC degradation (Figure 3.30).

Even though, the effect (either positive or negative) of higher temperatures were not verified in the present tested conditions, a positive effect in temperature (50 ºC) was found for oxalic at iridium anode (Scialdone et al., 2011). The authors highlight the fact that the effect of some operative parameters as temperature strongly depends on the nature of the electrode. Also (Saracco et al., 2001) found that the oxidation of coumaric acid was favored by higher temperatures (between 25 and 40 ºC) at Pt/Ti, PbO_2 and Ru/Ti. Still, more studies are needed to illustrate the mechanism of temperature influence on both mediated anodic oxidation and mediated oxidation at MMO anodes (Wu et al., 2014). All of the mentioned reasons above make the MMO circular mesh tested in the present work attractive for a full-scale operation.

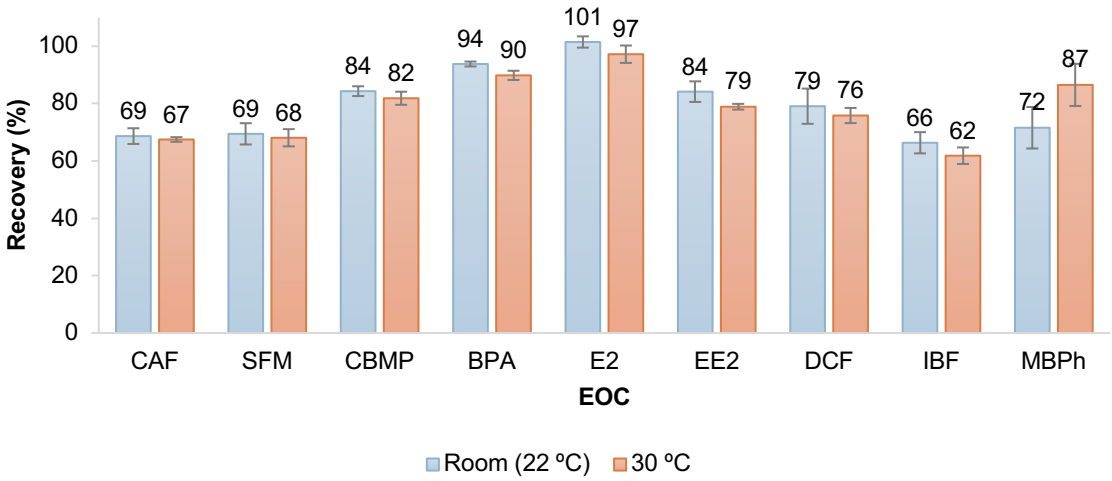


Figure 3.30 - Effect of temperature in EOC degradation (n=2).

- *Cathode influence*

The voltage, pH and conductivity are shown in Table 3.23.

Table 3.23 - pH, conductivity and voltage drop for the EK treatment using MMO circular mesh as anode and cathode (n=4).

EK#	pHi	pHf	Condi (mS/cm)	Condf (mS/cm)	Voltage initial	Voltage final
EK 6.1	8.05	8.42	1.15	1.13	10.7	10.0
EK 6.2	8.05	8.42	1.15	1.01	11.4	10.8
EK 6.3	7.91	7.74	1.18	1.01	9.8	10.1
EK 6.4	7.91	7.74	1.18	1.04	9.3	9.6

The removals of EOC are presented in Figure 3.31. The MMO circular mesh both as anode and cathode showed removals between 74% ±15 and 94% ±8. Comparing with the MMO bar as cathode, significantly differences (p<0.05) were found for the EOC that showed to be more difficult to remove: CAF and CBMP (35% and 50% of difference comparing with MMO bar, respectively). It was expected that the degradation of the compounds would increase with a higher surface area-to-volume ratio as stronger reactions are provided between the electrodes and the compounds may suffer anodic oxidation and/or cathodic reduction. These results indirectly demonstrate that anodic oxidation power was not the only reason for the different degradation rate and that cathode material and shape can affect organics degradation by reduction reactions (Chu et al., 2012).

In previous works, the choice of cathode also showed to have a significant influence on the efficiency of the process, particularly for H_2O_2 accumulation and Fe^{2+} regeneration. In a divided electrolytic system (Yuan et al., 2013) reported a minimal degradation of BPA in anodic compartment with addition of Fe^{2+} ruling out the contribution of anodic oxidation and the production of H_2O_2 at the MMO anode. In comparison, the degradation was significant in the cathodic compartment in the presence of Fe^{2+} and O_2. The minimal degradation in the cathodic compartment in the absence of Fe^{2+} and O_2 proves that BPA cannot be reduced by the direct cathodic reduction. But instead, H_2O_2 was produced from the reduction of O_2 on Ti/MMO cathode, thereby contributing to BPA degradation in the presence of Fe^{2+}.

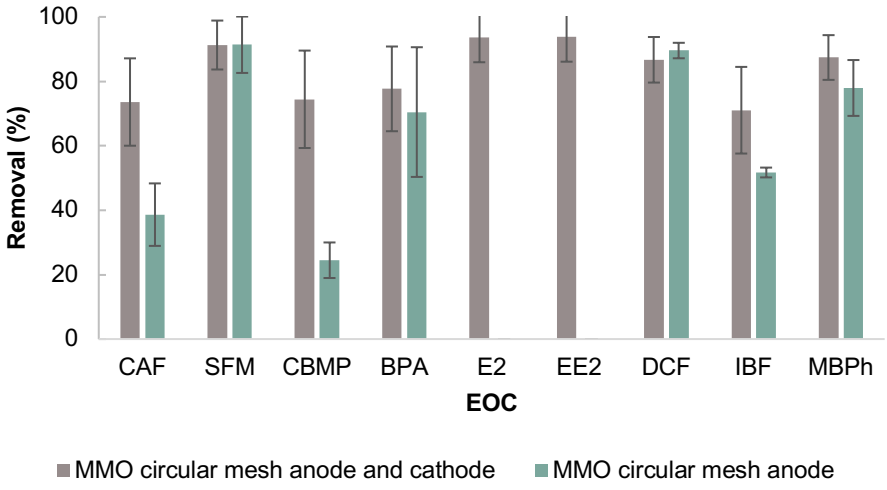


Figure 3.31 - EOC removals (%) by EK using MMO circular mesh as anode and cathode (n=4).

According to experimental data, the degradation curves of CAF, CBMP, SFM showed similar behavior following a first-order kinetics with correlations (R^2) between 0.9751 and 0.9934.

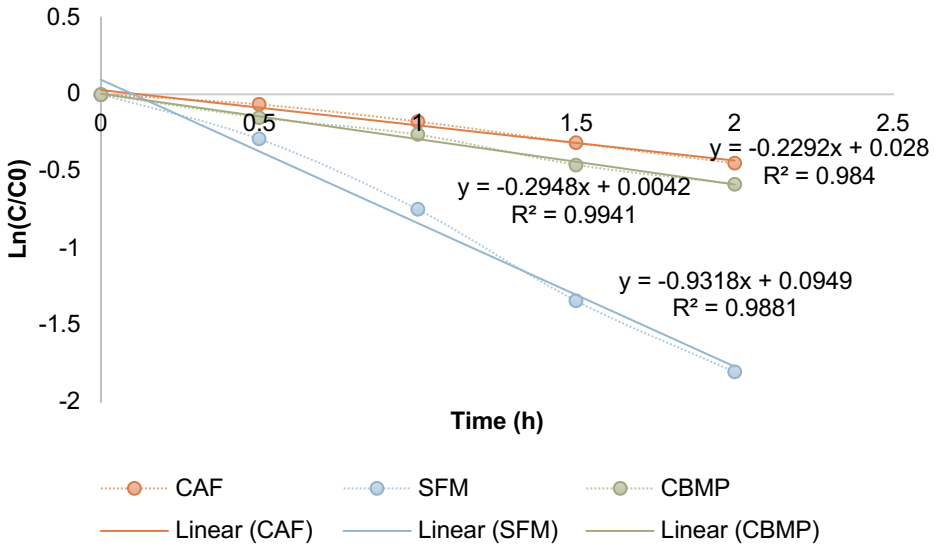


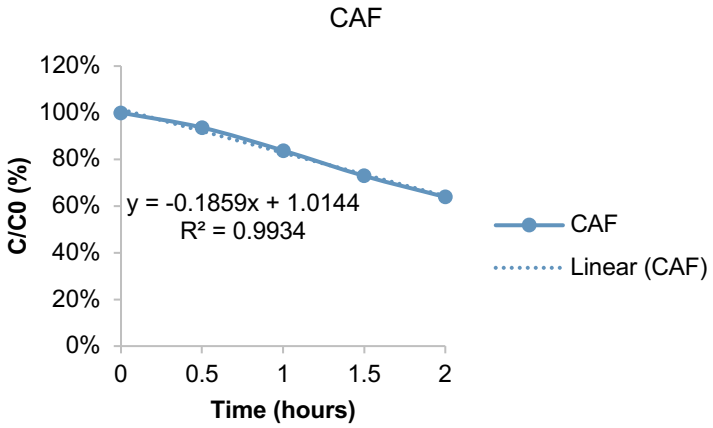
Figure 3.32 - Pseudo-first order kinetics for CAF, SFM and CBMP.

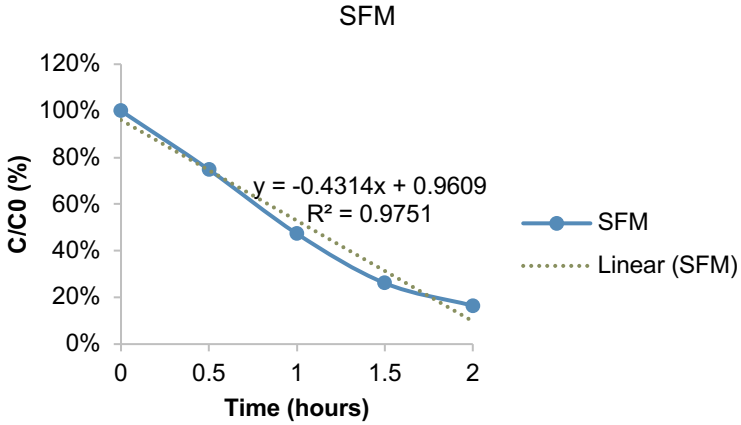
On the contrary, BPA, E2, EE2, IBF and DCF had a fast-initial degradation within the first half an hour slowly decreasing until the end of the experiments, without following any kinetic equation related to simple reaction orders (R^2 ranged between 0.53 and 0.71). The constant of velocity (k) present in Table 3.24 was calculated assuming a pseudo-second order reaction. This kind of reaction was reported to be rarely seen in electrochemical oxidation of organics in water, and the explanation is at present time not evident (Muff and Søgaard, 2010). The evolution of the normalized concentration of EOC along the EK experiment using MMO circular mesh as anode and cathode is shown in Figure 3.33 for each EOC.

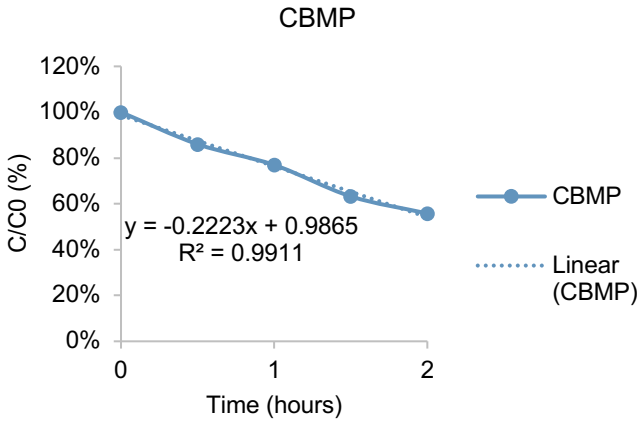
Table 3.24 - Pseudo first-order kinetics (ln(C0/C) =−kt) of EOC removal through (k x10^{-2} h^{-1}).

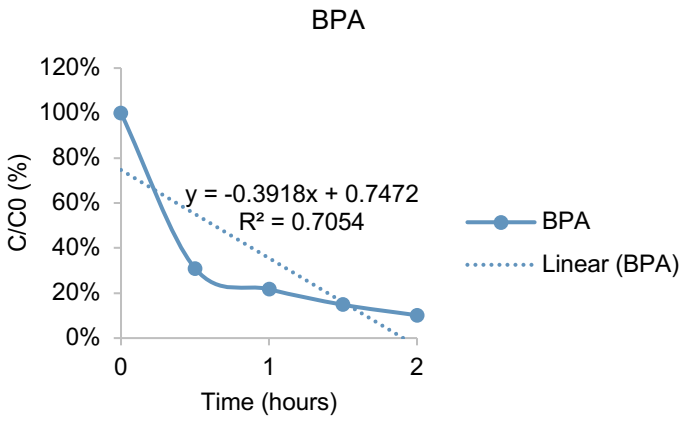
	CAF	SFM	CBMP	BPA*	E2*	EE2*	DCF	IBF*	MBPh
k (s^{-1})	0.22	0.90	0.29	4.93	14.27	11.71	0.75	6,49	0.67
R^2	0.99	0.98	0.99	0.71	0.65	0.70	0.85	0.53	0.99

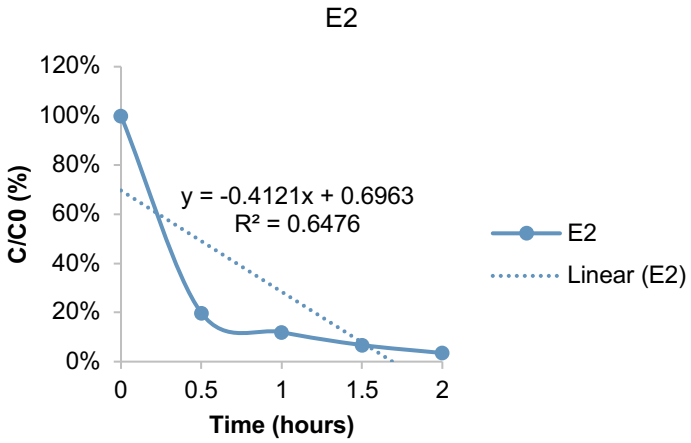
*assuming a pseudo-second order reaction kinetics k (M^{-1} s^{-1})
The values in blue mean R^2<0.85

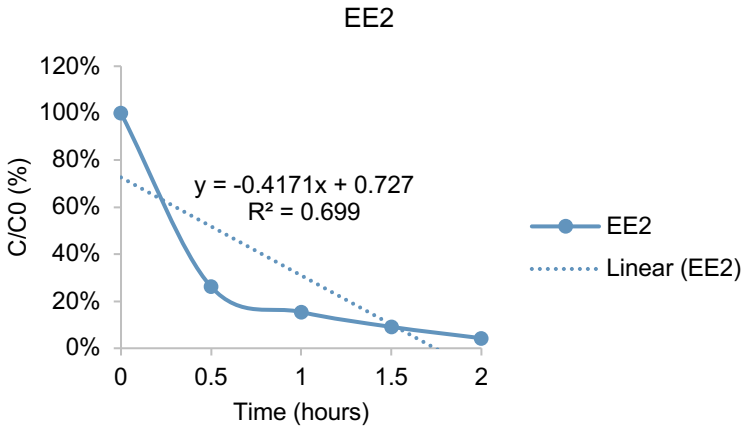

CAF
120%
100%
80%
60%
40%
20%
0%
C/C0 (%)
y = -0.1859x + 1.0144
R² = 0.9934
0
0.5
1
1.5
2
Time (hours)
CAF
Linear (CAF)


SFM
120%
100%
80%
60%
40%
20%
0%
C/C0 (%)
y = -0.4314x + 0.9609
R² = 0.9751
0
0.5
1
1.5
2
Time (hours)
SFM
Linear (SFM)


CBMP
120%
100%
80%
60%
40%
20%
0%
C/C0 (%)
y = -0.2223x + 0.9865
R² = 0.9911
0
1
2
Time (hours)
CBMP
Linear (CBMP)


BPA
120%
100%
80%
60%
40%
20%
0%
C/C0 (%)
y = -0.3918x + 0.7472
R² = 0.7054
0
1
2
Time (hours)
BPA
Linear (BPA)


E2
120%
100%
80%
60%
40%
20%
0%
C/C0 (%)
y = -0.4121x + 0.6963
R² = 0.6476
0
0.5
1
1.5
2
Time (hours)
E2
Linear (E2)


EE2
120%
100%
80%
60%
40%
20%
0%
C/C0 (%)
y = -0.4171x + 0.727
R² = 0.699
0
0.5
1
1.5
2
Time (hours)
EE2
Linear (EE2)

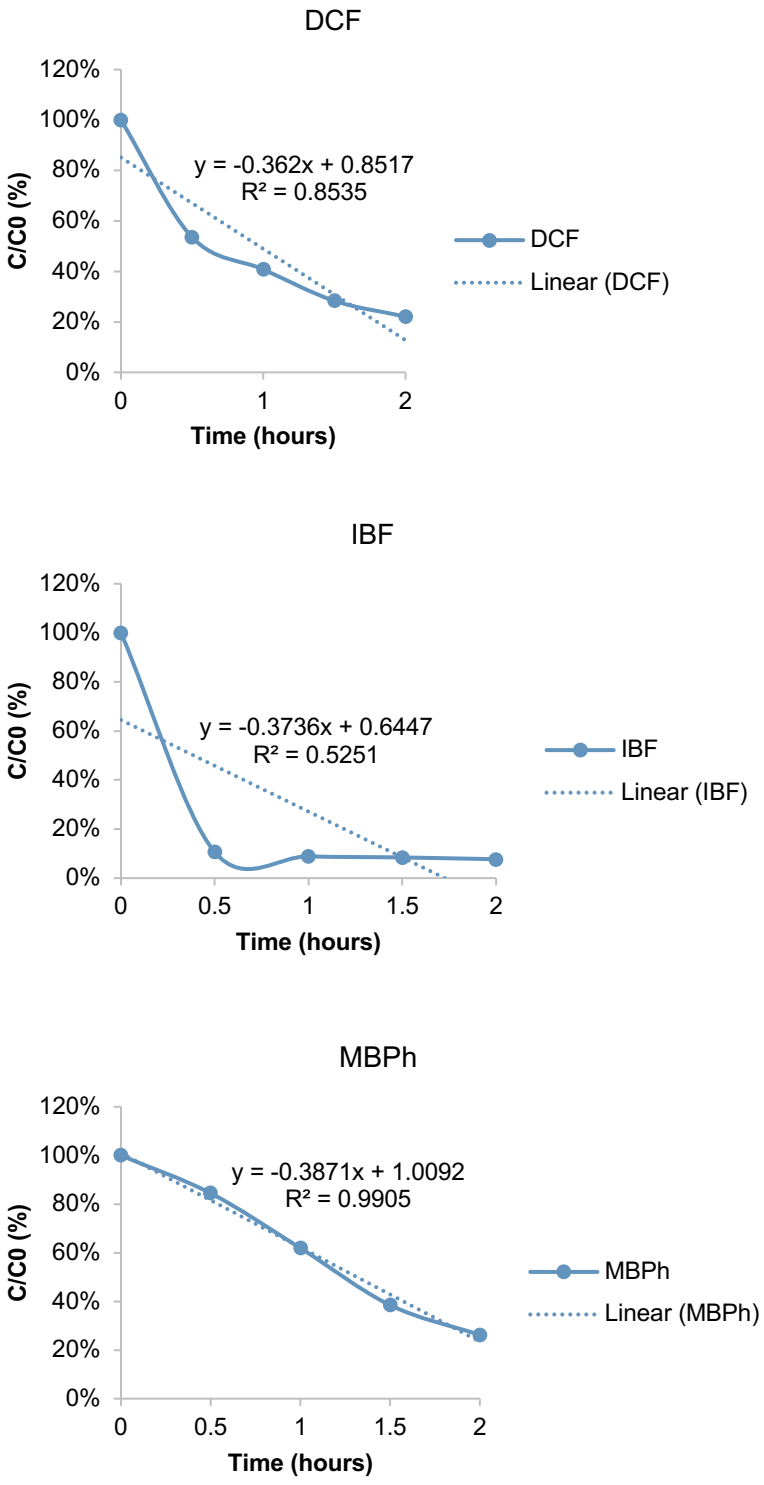


Figure 3.33 - The evolution of the normalized concentration of EOC along the EK experiment using MMO circular mesh as anode and cathode for the nine EOC in study.

3.5.4.5. Proof-of-concept

The final set-up was decided having in mind the results previously obtained. The optimum operating conditions were set using the MMO circular mesh both as anode and cathode applying a current intensity of 175 mA and running in batch of 2 hours each to treat 900 mL of effluent. Despite the doubled size, the same EOC removal efficiency was achieved, up to 90% for all the EOCs under study. The pH, conductivity and voltage drop are in Table 3.25.

Table 3.25 - pH, conductivity and voltage drop for the proof-of-concept (n=2).

pHi	pHf	Condi (mS/cm)	Condf (mS/cm)	ΔV (V)
7.82	7.75 [1]	1.40	1.33	0.1
7.82	8.24 [1]	1.40	1.26	0.2

[1] at 21.9 ºC

Once the EK treatment revealed positive results in the EOC removal, as described earlier, a prototype should be implemented in a WWTP as a tertiary effluent treatment. Besides the technical feasibility, the economic feasibility needs to be also considered for any technology to be suitable for use in the industry. To scale up the reactor in this study, the initial investment cost is not considered to be high as it needs a tank, electrodes and a power supply that can be connected to a solar panel. Comparing with the other electrode materials, one of the attractive advantages of the MMO electrodes, besides the high versatility, is the high energy efficiency and cost-effectiveness.

This can be verified when comparing to the energy consumption of Pt/Ti electrodes. The energetic consumption was calculated through the following equation and the results are shown in Table 3.26.

$$\boldsymbol{Energy\ consumption\ (kWh)} = \frac{\boldsymbol{V \times A \times h}}{\boldsymbol{1000}}$$

V = cell voltage average, Volts
A = applied current, Amps
h = time of treatment, hours

Even using the MMO material, when replacing the bar to MMO circular mesh, the energy consumption spent went down 1.7 times than when using a bar. This will positively reflect in the energy costs: 0.7 €/kWh instead of 1.1€/kWh. The MMO mesh circular in both anode and cathode has the energy consumption average of 0.7 €/m^3 of effluent, which means 2.5 times less than using Pt/Ti. The use of mesh to have less energy consumption than using Pt/Ti bar in EK was also observed by (Parés Viader et al., 2016). Comparing with other treatments, also based on compounds oxidation, namely advanced oxidation process the EK treatment proposed can be cheaper. (Mahamuni and Adewuyi, 2010) summarized the costs for various AOPs. e.g., US + UV + H_2O_2 was found to be the most economical ultrasonic process for waste water treatment containing reactive azo dye. The cost of the waste water treatment containing reactive azo dyes using this process was $65.17/1000 gallon.

Summing up the process under study has the main advantages of being: (i) simple to operate and to design; (ii) without addition of any reagent; (iii) handling low EOC concentrations; (iv) batch processes

in very short periods of time; (v) low investment cost; and (vi) possibility of water reuse (more studies are needed in order to guarantee all the regulated parameters).

Table 3.26 - Energetic costs for each effluent treatment by EK technology testing different anode materials.

Goal	Anode material; shape	Cathode material; shape	Voltage average (V)	Current intensity (A)	Energy consumption (kWh) (average values)	€/m³ (*)	€/m³ (average values)
Anode performance	MMO; bar	MMO; bar	26.35	0.1	0.00513	**1.8**	**1.7**
	MMO; bar	MMO; bar	26.30	0.1		1.8	
	MMO; bar	MMO; bar	27.95	0.1		1.9	
	MMO; bar	MMO; bar	22.10	0.1		1.5	
	Pt/Ti; bar	MMO; bar	28.25	0.1	0.00528	1.9	**1.8**
	Pt/Ti; bar	MMO; bar	28.45	0.1		1.9	
	Pt/Ti; bar	MMO; bar	24.65	0.1		1.6	
	Pt/Ti; bar	MMO; bar	24.30	0.1		1.6	
	Pt/Ti; Mesh	MMO; bar	22.50	0.1	0.00449	1.5	**1.5**
	Pt/Ti; Mesh	MMO; bar	22.65	0.1		1.5	
	Pt/Ti; Mesh	MMO; bar	22.25	0.1		1.5	
	MMO; Mesh	MMO; bar	19.9	0.1	0.00388	1.3	**1.3**
	MMO; Mesh	MMO; bar	18.8	0.1		1.3	
	MMO; Mesh	MMO; bar	20.95	0.1		1.4	
	MMO; Mesh	MMO; bar	18.05	0.1		1.2	
	MMO; circular mesh	MMO; bar	18.7	0.1	0.00342	1.2	**1.1**
	MMO; circular mesh	MMO; bar	16.5	0.1		1.1	
	MMO; circular mesh	MMO; bar	17.8	0.1		1.2	
	MMO; circular mesh	MMO; bar	15.35	0.1		1.0	
Cathode influence	MMO; circular mesh	MMO; circular mesh	10.35	0.1	0.00207	0.7	**0.7**
	MMO; circular mesh	MMO; circular mesh	11.10	0.1		0.7	
	MMO; circular mesh	MMO; circular mesh	9.95	0.1		0.7	
	MMO; circular mesh	MMO; circular mesh	9.95	0.1		0.7	
Proof-of-concept	MMO; circular mesh	MMO; circular mesh	7.15	0.175	0.00247	0.4	**0.4**
	MMO; circular mesh	MMO; circular mesh	7.00	0.175		0.4	

(*) Considering an energy price of 0.15 €/kWh
Voltage average: average between initial and final voltage in the EK treatment

3.5.5. Integrated EK/ED treatment with 1C and 2C-cells

Nine EOC were study: CAF, SFM, CBMP, BPA, E2, EE2, IBF, DCF and MBPh.

The results from ED experiments (Section 3.5.2; also in (Ferreira et al., 2018)) showed that it was possible the simultaneous removal EOC and P recover. However, optimization of the process was still needed.

The best set-up was using AEM and with effluent in anode compartment. The removals of the five EOC studied were 71% (BPA, E2, EE2 and MBPh) and less for CAF (57%). Having also in mind the results obtained from EK set-ups tested, the present work aimed to combine both and provide a batch treatment method and apparatus for simultaneous EOC removal and phosphorus recover from effluent for further reuse in agriculture. The effluent in cathode compartment using AEM, was also tested in this work because the safe effluent discharge in aquatic bodies needs to be also considered.

For this purpose, three integrated treatments were thought combining 2C- and 1C-cell.

Regarding general parameters (Table 3.27), the treated effluent pH showed to be very alkaline when placed in cathode compartment (10<pH<12) and decreased to 6.21 when placed in anode. Comparing with the initial values (Appendix 3), the effluent conductivity decreased when placed in cathode and using AEM due to the migration of anions towards anolyte.

Table 3.27 - pH, conductivity and voltage drop for EK/ED sequential steps working in batch mode.

	Final pH		Final conductivity		Voltage	
EK set-up	**Effluent**	**Electrolyte**	**Effluent**	**Electrolyte**	**Initial**	**Final**
1C + C.AEM	10.61	2.15	0.42	3.16	9.8/15.4	9.3/14.3
1C + C.AEM + 1C	11.67	2.33	0.99	2.90	17.5/24/11.3	15/14/13.8
A.AEM + 1C	6.21	11.94	1.13	1.59	22.4/8.3	13.5/13

Legend:
1C: 1 compartment
A.AEM: effluent placed in anode compartment using anion exchange membrane
C.AEM: effluent placed in cathode compartment using anion exchange membrane

In ED experiments (results shown in Section 3.5.2.2.) CAF showed to be less susceptible to suffer electrodegradation not being removed when the effluent was placed in the cathode compartment. Thus, a set-up where CAF showed to be highly removed (1C-cell, in *Section 3.5.4.2. EOC removal*) following a step where P could still be recovered in electrolyte showed to be an option if the aim is to discharge the effluent. In the cathode, the pH of the effluent increased to values above compounds pKa, except for CAF (pKa=14), which is present as neutral. This means that BPA, E2, EE2 and MBPh suffered deprotonation, being mainly present as anions, being thus able to electromigrate to the anode compartment through the AEM in the experiment C.AEM. For E_{1C+2C} the idea was first to promote the degradation of the EOC, previously tested, with the step of P recovering. Still, CAF and CBMP are more recalcitrant to oxidation and reduction reactions (69% of removal) and P was not found in anolyte. For $E_{1C+2C+1C}$ more time was given for the P mobilization and 2.2 mg L^{-1} of P migrated from effluent to electrolyte for 4 hours, which means 76% of P recovered. The acid pH promotes neutral or monovalent phosphate forms (H3PO4/ H2PO_4^-), whereas in cathode compartment, the pH of the effluent becomes alkaline (>8), where phosphates are mostly present in their divalent and trivalent anionic forms (HPO_4^{2-}/PO_4^{3-}), which facilitates their electromigration towards the anode compartment.

Comparing with the previous set-up, an extra step (1C) was added to the 1C + C.AEM in order to improve EOC removals. Regarding to EOC removal, even more time was given for the experiment (2h + 4h + 2h; 8 hours in total), the degradations did not increase (except for DCF, where 20% more removal

was registered). In this set-up three steps were performed: oxidation and reduction reactions at the same time with a 2C step in between.

With effluent placed in anode compartment a very acidic effluent pH was excepted in the end of the experiment, which is a disadvantage for further reuse. With the 1C step, the removals improved showing approx. 100% of CAF and CBMP removal (more 30% than the other set-ups tested in this Section) that showed to be more resistant to be removed by electrochemical process. All the other EOC showed removals above >95%, except IBF (72%). The production of hydrogen peroxide is well known to play an important part on the treatment efficiency of organic contaminants removal and in this set-up H_2O_2 was detected (>25 mg L-1) after 30 min of experiment in the effluent compartment.

In electrolyte, even though at very low percentage (1%), CAF, CBMP and IBF were able to pass through AEM towards electrolyte. However, as using A.AEM set-up the P does not migrate to anolyte, which allows effluent reuse in agriculture.

The results in this section are considered preliminary and more studies (including to do replicates) are needed.

Table 3.28 - Removal rate of EOC from effluent for the combination between 1 and 2C-cell.

EK set-up	CAF	SFM	CBMP	BPA	E2	EE2	IBF	DCF	MBPh
1C + C.AEM	69	92	69	85	88	90	88	76	90
1C + C.AEM + 1C	64	99	71	95	87	99	**99**	**96**	98
A.AEM + 1C	**97**	**100**	**100**	**< LD**	**< LD**	**< LD**	72	90	**99**

Legend:
AEM: anion exchange membrane;
2-compartments cell:
A.AEM: effluent placed in anode compartment using AEM;
C.AEM: effluent placed in cathode compartment using AEM.
Bold values mean the highest removal and the red the lowest; and the red values mean the lowest removals.

SECTION IV

4. CONCLUSIONS

Soil

Electro-based technologies were feasible to remove the legacy contamination in soil of As, oil and EOC:

- **The ED treatment of As-contaminated soil** showed removals in the range of 400-478 mg kg^{-1}, corresponding to 50-80% of the initial As content. The pre-treated soil (washed with flocculant addition) showed higher (p<0.05) As concentration but higher removals rates were not achieved, as it was mainlyin residual and oxidizable forms present after ED process. The comparison between 14, 7 and 3 days of ED remediation showed that As was mostly (approx. 60%) desorbed from soil within the first 3 days, but a longer period is required for As to cross the AEM towards the anolyte. Even though at the end of the EK treatment, As levels were above of the regulatory criteria, the experimental results showed that the treated soil can be potentially used for building materials, without risk of leaching.

- **The polar soil** showed a **TPHs** concentration of 69,500 mg kg^{-1}, which decreased up to78% after 14 days of remediation. The effect of the current was not observed in the tested conditions as the control showed similar removals to EKR due to natural attenuation. Among the EKR experiments, the effect of the current showed to be lower (~30%) in the anode at room temperature compared to cold temperature. Higher removals were found in cathode side, which can be potentially justified by the cold-adapted microorganisms, naturally present in the Sisimiut soil, that showed to have influence in PHs degradation in the control sample (without applied electric current, in cold conditions). The electric current strategies applied showed to be an option to explore in order to maintain the soil parameters (e.g. almost no pH changes) in cold climate conditions.

- **EOC removal**
    - **For soil slurry, the EK/ED** also showed to be a promising technology to remove EOC, with removals between 44% and 100% (through mobilization and/or degradation) after 72h of treatment. The cell design showed to have an influence in contaminants removal. Using cells with divided compartments (3C or 2C), BPA and MBPh were mainly mobilized towards the anode compartment through the action of an electric field, whereas EE2 suffered degradation. However, when soil slurry was placed in the cathode compartment (2C-cell design) degradation of MBPh overcomes its mobilization, which can be explained by pH changes (pH soil slurry > pKa of MBPh). The use of a cell with one compartment (1C-cell) showed to be the best option for homogeneous degradation rates of the contaminants under study. Experimental data suggests that 1C-cell design may have broader application range for contaminants with different physical and chemical characteristics. Its main advantage is its simplicity:

EOC are remoedl by degradation (>44%) instead of their mobilization to the electrode compartment, which would require further treatment of the electrolyte.

- **In EK-soil remediation**, the electric current showed to enhance the removals of EOC in 40% comparing with control (without electric current). As happened in EK experiments with PHs, there was also a tendency for higher removals in cathode side with statistical significance differences (p<0.05) for some EOC. The central compartment showed higher EOC concentrations, mainly for IBF and DCF, meaning that contaminants were probably mobilized and, due to changes in soil characteristics i.e. pH, the EOC accumulated in the central section. Regarding to electric current strategies, swithich On/Off combined with REP showed to be the most suitable strategy as did not change the soil characteristics in terms of pH, and more equal remediation in the differente compartments (anode, central and cathode) for the six EOC was achieved.

Effluent

- **Cws** with *S.maritima* as a specie of plant and LECA as a substrate showed to be a green technology to remove EOC. Removals ranged between 44 – 97% for 7 days, and the efficiency was maintained between successive cycles suggesting that the studied components have the potential to remove EOC in a continuous way.

The results showed that EK/ED is a promising technology, with potential to be integrated in WWTPs as a polishing step for EOC removal from effluent:

- **The removals by the 2C-cell designs** showed that the type of membrane (AEM vs. CEM) and the location where the effluent is placed influenced the removal of EOC. Removals were higher when using an AEM (60–72%) than a CEM (8–63%), except for CAF when the effluent was placed in the cathode compartment, that did not show any removal. When using an AEM with the effluent placed in the anode compartment, all the EOC (including caffeine) were removed between 57–72%, mainly through electrodegradation phenomena. Regarding phosphorus, the present results showed that ED is a promising technology for its recycling, with the best results achieved when AEM were used. At the same time, the studied setup provides flexibility, as it allows to choose the polarity of the electrode in contact with the effluent, depending on the final use: (i) anode for agricultural irrigation, so that phosphorus remains in the effluent or (ii) cathode in case of discharge of the effluent to receiving waters, so that remaining P is recovered in the electrolyte (anode). Thus, a simultaneous removal of EOC and recovery of P were proved to be possible and optimization of the process was further carried out;

- **With a single EK reactor (1C-cell)** higher EOC removals were achieved; horizontal and batch mode showed to be more efficient in terms of EOC removal than vertical and continuous flow mode; both the electrodes' shape and material showed to be important parameters to improve the EK process. Not only for the EOC removal, but also to make a more efficient process in

terms of energy consumption. The optimization of the current density applied to the 1C-cell was also particularly important, as the increase of the current density does not necessarily mean higher EOC and more efficient process. The proof-of-concept was carried out with almost complete remediation of all the nine EOC (90%). The results achieved in this study show a different perspective from previous studies regarding the MMO anode material;

- **The combination of 1-C (EK reactor) combined with 2C-cell** allowed simultaneous (i) removal of EOC (90%, except for IBF (75%)) and (ii) P recovery.

In general, the studied electro-based technologies showed a successful removal of legacy contamination from soil and several EOC contaminants with very different characteristics from effluent. The removals were strongly dependent of contaminants characteristics and EK/ED tested conditions. However, electro-based technologies showed, in the present Ph.D. work, to be a versatile technology. In addition to achieve good removals, EK/ED can be considered a green technology since no additional chemicals are required and energy demands can easily be covered by renewable production means like solar panels. Also, the estimated costs of the applied technology would potentially decrease either through the use of different electrodes for effluent or through electric current strategies (periodic electric current and reversed electrode polarization) for soil.

5. FUTURE DEVELOPMENTS

Soil

- The effect of the current in extreme weather conditions (cold temperatures) should be more explored as these environments are sensible and may benefit with remediation technology as an answer to unexpected loads of contamination;
- Regarding effluent soil irrigation, several cycles during a longer period should be tested to assesses EKR performance in mitigating the presence of EOC, either horizontally or vertically;
- Also, since effluent vary greatly in biological-physical-chemical properties, a systematic understanding of the interactions between water matrix components and EOC is necessary.
- A comprehensive evaluation of the risk from the presence EOC in soil must not be limited to the assessment of environmental behavior of the parent compound, but also requires investigation of the behavior of metabolites;
- Test the EK as a *in situ* remediation technology system with mixed contamination (heavy metals and organic compounds);

Effluent

- The electro-chemical reactor (either 1C or the combination between 1C and 2C) with the optimized technologies need to be tested in up-scale;
- Study the electro-degradation EOC to: (i) assess the formation of possible by-products or confirm the complete degradation (mineralization) of the compounds and (ii) propose degradation pathways;
- The knowledge on the evolution of Cl^- ion and chlorinated species, BOD_5 and COD are of great interest and necessary to evaluate the viability of the proposed EK technology;
- The microbiology of effluent before and after EK process should be studied;
- The CW systems enhanced by electro-based technologies should be explored and processes of EOC removal completely understand; microbial fuel cells to potentiate the remediation could be also a topic to explore.

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APPENDICES

Appendix 1 - List of the emerging organic contaminants in common and more detected in Spain, France and Portugal. (in bold are the EOC selected for the present work)

	Emerging organic contaminants (EOC)	Category	SP	FR	PT	Frequency of detection (%)		
1	**Ibuprofen**[1]	Anti-inflammatory	x	x	x	100	100	89
2	Atenolol[1]	β-blocker	x	x	x	100	100	44
3	**Diclofenac**	Anti-inflammatory	x	x	x	62	100	22
4	Ketoprofen	Anti-inflammatory	x	x	x	29	53	55
5	**Carbamazepine**	Anticonvulsant	x	x	x	3	72	11
6	**Sulfamethoxazole**[2]	Antibiotic	x	x	x	15	39	11
7	Clarithromycin[2]	Antibiotic	x	x	x	6	100	44
8	Venlafaxine	Antidepressant		x	x	-	100	100
9	Salicylic acid[1]	Analgesic	x		x	100	-	100
10	Sotalol	β-blocker	x	x		5	100	-
11	Tonalide	Fragrance		x	x	-	100	100
12	Trimethoprim[1]	Antibiotic	x	x		3	100	-
13	Codeine[1]	Analgesic	x			100		
14	Propyphenazone[1]	Analgesic and antipyretic	x			100		
15	Ranitidine[1]	Antiulcer	x			100		
16	Benzoylecgonine	Drug (coicaine metabolite)	x			26		
17	Benzofenone 1	UV filter	x			6		
18	Paracetamol	Anti-inflammatory	x			6		
19	**Benzofenona 3**	UV filter	x			3-5		
20	Imidacloprid	Insecticide	x			5		
21	Acebutolol	β-blocker		x		100		
22	Diazepam	Tranquilizer		x		100		
23	Erythromycin[2]	Antibiotic		x		100		
24	Metoprolol	β-blocker		x		100		
25	Niflumic acid	Analgesic and anti-inflamatory		x		100		
26	Ofloxacin	Antibiotic		x		100		
27	Roxithromycin[2]	Antibiotic		x		100		
28	Sotalol	β-blocker		x		100		
29	Tramadol	Analgesic		x		100		
30	Galaxolide	Fragrance			x			100
31	Cashmeran	Fragrance			x			100
32	Dimethyl Aminophenazone	Analgesic, anti-inflammatory, antipyretic			x			67
33	**Caffeine**	Stimulant			x			44
34	Amoxicilin	Antibiotic			x			22
35	Enalapril	ACE inhibitors			x			33
36	Flurbiprofen	Anti-inflammatory			x			33
37	Fluticasone	Corticosteroid			x		33	
38	Paroxetine	Antidepressant			x		33	

The list of ECs in Portugal was based on research carried out by: Salgado R, Noronha JP, OehmenA, Carvalho G, Reis MAM. Analysis of 65 pharmaceuticals and personal care products in 5 wastewater treatment plants in Portugal using a simplified analytical methodology. WaterSci. Technol. 2010;62:2862–71;
The ECs data was provided by CENTA that conducted in collaboration with Agencia Andaluza de Medio Ambientey Agua (AMAYA) a study in 12 WWTPs in 2015.

Appendix 2 - Initial Total hydrocarbons present in Polar soil (n = 2).

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Ensaios

Boletim de Análise
Analysis Report

NOVA.ID.FCT - Associação p/ inovação e desenvolvimento da FCT Campus
Quinta da Torre
2829-516 MONTE DA CAPARICA

Ref. LABQUI: 07770/18
LABQUI Ref.: *07770/18*

BOL-LAB-0484/18-1.07770/18 **Boletim Definitivo - Revisão 0** **Divulgação:** Confidencial
BOL-LAB-0484/18-1.07770/18 ***Definitive report - Revision 0*** ***Diffusion:*** *Confidential*

Identificação: Solo SiSimint, Gronelândia com óleo
Identification:

Tipo de amostra: Solo
Sample type: *Soil*

Recepção: 16-04-2018
Received at: *16-04-2018*

Duração da análise: 04-05-2018 a 07-05-2018
Testing duration: *04-05-2018 to 07-05-2018*

Emissão do boletim: 07-05-2018
Report date: *07-05-2018*

Amostragem: Da responsabilidade do cliente
Sampling: *Client responsability*

Tipo: -----
Type: *-----*

Início: -----
Start: *-----*

Fim: -----
End: *-----*

Dados complementares:
Additional data:

Ensaio *Test* / *Norma Method*	**Resultado** *Result*	**Unidades** *Units*	**Limite de lei**	**VMR**
Óleos Minerais C10-C40 *Mineral Oils C10-C40* *PO.L.LABQUI-5.4/O070: Ed.A, Rev.02*	$7{,}0 \times 10^{4}$	mg/kg de matéria seca	-----	-----

'PO.L-LABQUI *' indica método interno do laboratório baseado, se indicado, no(s) documento(s) normativo(s).
*'PO.L-LABQUI *' indicates internal method of LABQUI based, if listed, on regulatory document(s).*

Limites de lei segundo: -----
Law limits by: -----

Observações:
Comments:

O Limite de Quantificação (LQ) do LABQUI para a soma de parâmetros orgânicos (aplicáveis), corresponde ao LQ mais elevado dos resultados individuais apresentados.
The limit of quantification for the sum of organic parameters performed by LABQUI (if applicable) corresponds to the highest individual LOQ presented.
O resultado do LABQUI reportado para a soma de parâmetros orgânicos (aplicáveis), corresponde ao somatório dos valores quantificáveis apresentados.
The result for the sum of the organic parameters performed by LABQUI (if applicable) is the sum of individual quantifiable values shown.
O resultado para HTP Fracção (C10-C50) corresponde à soma dos valores quantificáveis apresentados para as cadeias: HTP Fracção (C16- C34), HTP Fracção (C10-C16) e HTP Fracção (C34-C50) ou ao LQ mais elevado dos resultados individuais apresentados para as cadeias mencionadas.
The result for TPH fraction (C10-C50) is the sum of quantifiable results of the fractions: TPH fraction (C16-C34), TPH fraction (C10-C16), and TPH fraction (C34-C50), or the highest limit of quantification presented for these chains, if not achieved quantifiable results.
VMA - Valor Máximo Admissível; VLE - Valor Limite de Emissão; VMR - Valor Máximo Recomendado; LQ - Limite de Quantificação.
MPV - Maximum Permissible Value; ELV - Emission Limit Value; RMV - Recommended Maximum Value; LQ - Limit of Quantification.
[a] - Ensaio não incluído no âmbito da acreditação.
[a] - Test not included in the scope of accreditation
[b] - Ensaio subcontratado acreditado no âmbito da acreditação do subcontratado e incluído no âmbito da acreditação do LABQUI.
[b] - Subcontracted test included in the scope of accreditation of the subcontractor and included in the scope of accreditation of LABQUI
[c] - Ensaio subcontratado acreditado no âmbito da acreditação do subcontratado e não incluído no âmbito da acreditação do LABQUI.
[c] - Subcontracted test included in the scope of accreditation of the subcontractor and not included in the scope of accreditation of LABQUI
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[e] - Ensaio subcontratado não incluído no âmbito da acreditação do subcontratado e não incluído no âmbito da acreditação do LABQUI.
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Responsável pela emissão de resultados
Responsible for issuing results

Tânia Santos
Responsável Técnico
Technical Director

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Ensaios

Boletim de Análise
Analysis Report

NOVA.ID.FCT - Associação p/ inovação e desenvolvimento da FCT Campus
Quinta da Torre
2829-516 MONTE DA CAPARICA

Ref. LABQUI: 07771/18 *LABQUI Ref.: 07771/18*
BOL-LAB-0484/18-1.07771/18 **Boletim Definitivo - Revisão 0** *BOL-LAB-0484/18-1.07771/18 Definitive report - Revision 0*
Divulgação: Confidencial *Diffusion: Confidencial*

Identificação: Solo SiSimint, Gronelândia com óleo - DP
Identification:

Tipo de amostra: Solo
Sample type: Soil

Recepção: 16-04-2018 *Received at: 16-04-2018*
Duração da análise: 04-05-2018 a 07-05-2018 *Testing duration: 04-05-2018 to 07-05-2018*
Emissão do boletim: 07-05-2018 *Report date: 07-05-2018*

Amostragem: Da responsabilidade do cliente
Sampling: Client responsability

Tipo: ----- *Type: -----*
Início: ----- *Start: -----*
Fim: ----- *End: -----*

Dados complementares:
Additional data:

Ensaio *Test* / *Norma Method*	**Resultado** *Result*	**Unidades** *Units*	**Limite de lei**	**VMR**
Óleos Minerais C10-C40 *Mineral Oils C10-C40* *PO.L.LABQUI-5.4/0070: Ed.A, Rev.02*	$6,3 \times 10^{4}$	mg/kg de matéria seca	-----	-----

'PO.L-LABQUI *' indica método interno do laboratório baseado, se indicado, no(s) documento(s) normativo(s).
*'PO.L-LABQUI *' indicates internal method of LABQUI based, if listed, on regulatory document(s).*

Limites de lei segundo: -----
Law limits by: -----

Observações:
Comments:

O Limite de Quantificação (LQ) do LABQUI para a soma de parâmetros orgânicos (aplicáveis), corresponde ao LQ mais elevado dos resultados individuais apresentados.
The limit of quantification for the sum of organic parameters performed by LABQUI (if applicable) corresponds to the highest individual LOQ presented.
O resultado do LABQUI reportado para a soma de parâmetros orgânicos (aplicáveis), corresponde ao somatório dos valores quantificáveis apresentados.
The result for the sum of the organic parameters performed by LABQUI (if applicable) is the sum of individual quantifiable values shown.
O resultado para HTP Fracção (C10-C50) corresponde à soma dos valores quantificáveis apresentados para as cadeias: HTP Fracção (C16- C34), HTP Fracção (C10-C16) e HTP Fracção (C34-C50) ou ao LQ mais elevado dos resultados individuais apresentados para as cadeias mencionadas.
The result for TPH fraction (C10-C50) is the sum of quantifiable results of the fractions: TPH fraction (C16-C34), TPH fraction (C10-C16), and TPH fraction (C34-C50), or the highest limit of quantification presented for these chains, if not achieved quantifiable results.
VMA - Valor Máximo Admissível; VLE - Valor Limite de Emissão; VMR - Valor Máximo Recomendado; LQ - Limite de Quantificação.
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Responsável pela emissão de resultados
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Tânia Santos
Responsável Técnico
Technical Director

Appendix 3 - Main physicochemical characteristics of the effluent collected after secondary treatment in WWTP.

	EFFLUENT SAMPLES								
Parameter (units)	S1	S2	S3	S4	S5	S6	S7	S8	S9
Color	Pale yellow	Pale yellow	Pale yellow	Yellow	Yellow	Yellow	Yellow	Pale yellow	Pale yellow
Odor	Very weak	Very weak	Very weak	Strong	Strong	Strong	Very weak	Very weak	Very weak
pH	8.00	8.01	7.84	8.29	7.82	8.05	7.91	8.02	7.90
Conductivity (mS cm^{-1})	1.23	1.10	1.26	1.45	1.40	1.15	1.18	1.11	1.00
Total phosphorus – P (mg L^{-1})	*NA*	3.40*	0.80	7.2*	0.84	4.60*	2.50*	2.9*	1.1
Total chloride - Cl^- (mg L^{-1})	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Total suspended solids - TSS (mg L^{-1})	30	**47**	20	68	20	**92**	< 10	< 10	< 10
Chemical oxygen demand - COD (mg O_2 L^{-1})	71	**139**	75	**175**	75	**258**	30	30	31
5-day biochemical oxygen demand - BOD_5 (mg O_2 L^{-1})	18	**50**	18	**70**	18	**45**	< 3	< 3	8.8
NH_4	*NA*	46.1*	41	*NA*	41	0.031	52.9*	*NA*	7
N total	*NA*	*NA*	39	*NA*	39	15	*NA*	*NA*	5.8

Notes:
NA: not analyzed
*Total phosphorus analysis was performed in HANNA Instruments Wastewater Multiparameter

Appendix 4 - Overview of the EK experiments carried out with effluent.

Goal	Experiment EK#	Cathode		Anode		Effluent sampling #	Current intensity (mA)
		Material	Shape	Material	Shape		
Anode performance	EK 1.1	MMO	Bar	MMO	Bar	1	100
	EK 1.2	MMO	Bar	MMO	Bar	1	100
	EK 1.3	MMO	Bar	MMO	Bar	2	100
	EK 1.4	MMO	Bar	MMO	Bar	4	100
	EK 2.1	MMO	Bar	Pt/Ti	Bar	1	100
	EK 2.2	MMO	Bar	Pt/Ti	Bar	1	100
	EK 2.3	MMO	Bar	Pt/Ti	Bar	3	100
	EK 2.4	MMO	Bar	Pt/Ti	Bar	4	100
	EK 3.1	MMO	Bar	Pt/Ti	Mesh	1	100
	EK 3.2	MMO	Bar	Pt/Ti	Mesh	1	100
	EK 3.3	MMO	Bar	Pt/Ti	Mesh	2	100
	EK 4.1	MMO	Bar	MMO	Mesh	2	100
	EK 4.2	MMO	Bar	MMO	Mesh	2	100
	EK 4.3	MMO	Bar	MMO	Mesh	2	100
	EK 4.4	MMO	Bar	MMO	Mesh	4	100
	EK 5.1	MMO	Bar	MMO	Circular mesh	2	100
	EK 5.2	MMO	Bar	MMO	Circular mesh	3	100
	EK 5.3	MMO	Bar	MMO	Circular mesh	3	100
	EK 5.4	MMO	Bar	MMO	Circular mesh	4	100
Current influence	EK 5.5.1	MMO	Bar	MMO	Circular mesh	4	125
	EK 5.5.2	MMO	Bar	MMO	Circular mesh	4	
	EK 5.5.3	MMO	Bar	MMO	Circular mesh	4	
	EK 5.5.4	MMO	Bar	MMO	Circular mesh	6	
	EK 5.6.1	MMO	Bar	MMO	Circular mesh	4	175
	EK 5.6.2	MMO	Bar	MMO	Circular mesh	6	
	EK 5.6.3	MMO	Bar	MMO	Circular mesh	6	
	EK 5.6.4	MMO	Bar	MMO	Circular mesh	7	
Cathode influence	EK 6.1	MMO	Circular mesh	MMO	Circular mesh	6	100
	EK 6.2	MMO	Circular mesh	MMO	Circular mesh	6	
	EK 6.3	MMO	Circular mesh	MMO	Circular mesh	7	
	EK 6.4	MMO	Circular mesh	MMO	Circular mesh	7	
Proof-of-concept	EK 7.1	MMO	Circular mesh	MMO	Circular mesh	5	175*
	EK 7.2	MMO	Circular mesh	MMO	Circular mesh	5	
Combination between 1 and 2C-cell	1C + C.AEM	MMO	Circular mesh	MMO	Circular mesh	8	175
	1C + C.AEM + 1C	MMO	Circular mesh	MMO	Circular mesh	8	
	A.AEM + 1C	MMO	Circular mesh	MMO	Circular mesh	9	

*splited in two

Appendix 5- LD and LQ and the correlation coefficient of the EOC analysis.

EOC	LD (ppm)	LQ (ppm)	R^2
CAF	0.3	0.9	0.9999
SFM	0.2	0.6	1.0000
CBMP	0.2	0.7	1.0000
BPA	0.3	0.8	0.9999
E2	0.2	0.5	1.0000
EE2	0.2	0.6	1.0000
IBF	0.7	2.2	0.9996
DCF	0.4	1.2	0.9999
MBPh	0.5	1.4	0.9998

LD = 3*standard deviation of the calibration
LQ = 3*LD
R^2 (correlation coefficient)

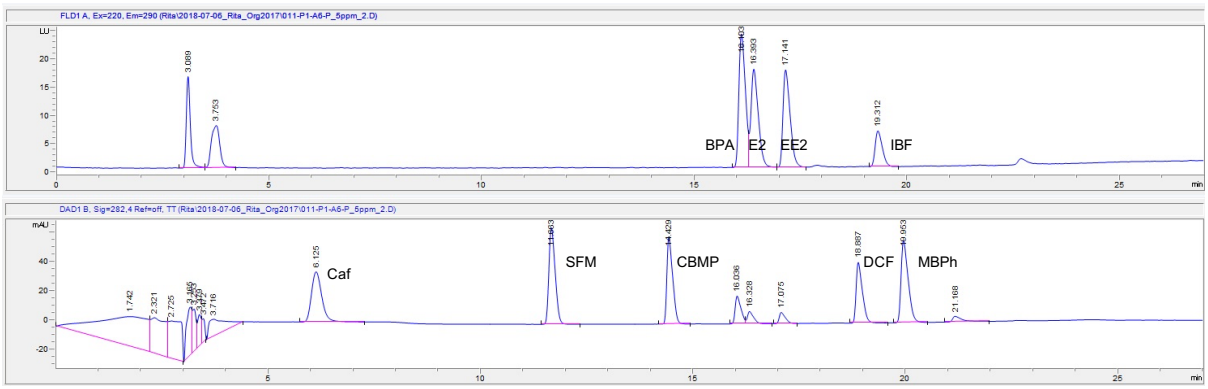
Appendix 6 - EOC recovery from effluent at T0h.

	EOC (%)								
n=2	**CAF**	**SFM**	**CBMP**	**BPA**	**E2**	**EE2**	**DCF**	**IBF**	**MBPh**
Effluent T0h_R1	83	85	99	70	92	100	86	85	83
Effluent T0h_R1	77	76	88	66	85	92	82	84	66
AVERAGE (%)	**80**	**81**	**94**	**68**	**88**	**96**	**84**	**85**	**75**
SD	3	4	5	2	4	4	1	0	8

Appendix 7 - EOC recovery from effluent at T2h.

	EOC (%)								
n=7	**CAF**	**SFM**	**CBMP**	**BPA**	**E2**	**EE2**	**DCF**	**IBF**	**MBPh**
Effluent T2h_R1	88	85	97	78	102	105	91	95	85
Effluent T2h_R2	82	84	101	76	96	106	92	97	76
Effluent T2h_R3	80	85	98	73	92	102	88	101	63
Effluent T2h_R4	87	87	105	76	103	106	97	98	77
Effluent T2h_R5	71	70	88	84	95	83	81	78	59
Effluent T2h_R6	95	95	103	71	108	109	101	84	75
Effluent T2h_R7	81	78	97	95	105	87	91	66	72
AVERAGE (%)	**84**	**85**	**99**	**76**	**99**	**102**	**92**	**92**	**73**
SD	7	7	5	8	5	10	6	12	8

Appendix 8 – Example of a chromatogram obtained from HPLC-DAD-FLD with the nine EOC in study (standart of 5 ppm).



PART II

PAPER I *Comparative assessment of LECA and Spartina maritima to remove emerging organic contaminants from wastewater*

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RESEARCH ARTICLE

Comparative assessment of LECA and *Spartina maritima* to remove emerging organic contaminants from wastewater

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Abstract The present work aimed to evaluate the capacity of constructed wetlands (CWs) to remove three emerging organic contaminants with different physicochemical properties: caffeine (CAF), oxybenzone (MBPh), and triclosan (TCS). The simulated CWs were set up with a matrix of light expanded clay aggregates (LECA) and planted with *Spartina maritima*, a salt marsh plant. Controlled experiments were carried out in microcosms using deionized water and wastewater collected at a wastewater treatment plant (WWTP), with different contaminant mass ranges, for 3, 7, and 14 days. The effects of variables were tested isolatedly and together (LECA and/or *S. maritima*). The presence of LECA and/or *S. maritima* has shown higher removal (around 61–97%) of lipophilic compounds (MBPh and TCS) than the hydrophilic compound (CAF; around 19–85%). This was attributed to the fact that hydrophilic compounds are dissolved in the water column, whereas the lipophilic ones suffer sorption processes promoting their removal by plant roots and/or LECA. In the control (only wastewater), a decrease in the three contaminant levels was observed. Adsorption and bio/rhizoremediation are the strongest hypothesis to explain the decrease in contaminants in the tested conditions.

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Keywords Constructed wetlands · *Spartina maritima* · LECA · Emerging organic contaminants · Wastewater

Introduction

Pharmaceuticals and personal care products (PPCPs) are daily discharged into the aquatic systems due to the general inefficiency of the conventional processes to remove emerging organic contaminants in wastewater treatment plants (WWTP). As a consequence, some PPCPs have been detected in aquatic environment at concentrations of about microgram per liter (Heberer 2002; Fent et al. 2006). Even in vestigial concentrations, these contaminants are of concern due to their potential ecological and environmental impacts (Pal et al. 2010).

One important aspect to decrease the mass of organic contaminants discharged into surface waters is the optimization of WWTP processes. Constructed wetlands (CWs), based on natural wetland systems, are an attractive technology for the removal of PPCPs from wastewaters due to their easy operation and maintenance, low-energy requirements, high rates of water recycling, and potential for providing significant wildlife habitat (Matamoros and Bayona 2006; Vymazal 2010; Zhang et al. 2014).

CWs are constituted by support matrix and plant species (Hijosa-Valsero et al. 2010). The substrates of CWs can be natural (e.g., gravel and sand) or an artificially modified natural material, like light expanded clay aggregates (LECA). LECA is considered a low-cost sorbent and exhibits a high sorption capacity for pharmaceutical compounds (removals of 48–97%) (Dordio et al. 2009, 2010) and herbicide (removal of 56–97%) (Dordio and Carvalho 2013). Despite the potential of LECA to remove these lipophilic compounds (Log K_{ow} between 1.37 and 3.97), its capacity is unknown to simultaneously remove a mixture with lipophilic and

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hydrophilic compounds. Also, there is limited knowledge about LECA efficiency in removing a successive arrival of PPCPs to CWs.

Different salt marsh plant species, such as *Phragmites australis* and *Typha latifolia*, have been used for pharmaceutical removal in CWs (Dordio et al. 2010; Carvalho et al. 2012). Other plant species may be used for this purpose being a valuable option to enlarge the range of applications in CWs. *Spartina maritima* has high tolerance to different salinity levels (e.g., 0, 171, and 510 mM NaCl) and capacity to react to climate changes (Adams and Bate 1995; Mateos-Naranjo et al. 2010) being an option to be used in WWTPs. *S. maritima* contributes to heavy metal removal (Reboreda and Caçador 2007; Duarte et al. 2009), but as far as we could ascertain, there is limited information about its potential to remove PPCPs.

The aim of the present work was to evaluate the capacity of CWs having LECA as a support medium and planted with *S. maritima* to remove from wastewater a mixture of lipophilic and hydrophilic compounds. The target compounds were caffeine (CAF), oxybenzone (MBPh), and triclosan (TCS), chosen based on their worldwide consumption, physicochemical properties, and chemical classes (Table 1). A fed-batch mode was simulated with pulses of contaminants' addition throughout the experiment (controlled experimental microcosm).

Materials and methods

Reagents and material

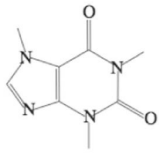
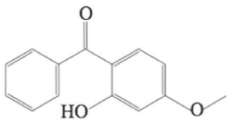
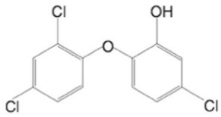
CAF (≥90%), MBPh (≥90%), TCS (Irgasan, ≥97%) were purchased from Sigma-Aldrich (Steinheim, Germany). Methanol (MeOH), acetonitrile (ACN), and acetone (ACE) were HPLC grade from Riedel-de Haën (Germany). All aqueous solutions were prepared with Milli-Q water. The standard solutions with the three compounds CAF, MBPh, and TCS were prepared in methanol (MeOH).

Light expanded clay aggregates (LECA), which were used for the support matrix of the CWs, had a size range between 3 and 8 mm and were supplied by ARGEX® (Portugal). LECA was washed several times with Milli-Q water and the liquid phase of the assay (deionized water or wastewater), to reduce the amount of fine materials and embed in the matrix.

Wastewater collection

The wastewater samples were collected after the secondary settling tank in a WWTP from Águas de Lisboa e Vale do Tejo Group located in Quinta do Conde, Sesimbra, Portugal (38° 34′ 13″ N, 9° 2′ 7″ W). The WWTP has the capacity to treat in the project horizon 19,300 m^3 day^{-1} of urban wastewater, corresponding to about 94,000 equivalent inhabitants.

Table 1 The physicochemical properties of the studied PPCPs

Compound	CAF	MBPh	TCS
Function	Central nervous system stimulant	Sunscreen agent	Antiseptic
Structure			
Molecular weight (g mol^{-1})	194.19	228.24	289.55
Solubility in water (mg L^{-1} at 25 °C)	2.16×10^4	69	10 (at 20 °C)
pKa (24 °C)[a]	14.4	7.6	7.9
Log K_{ow}[b]	-0.07	3.79	4.76

References: http://pubchem.ncbi.nlm.nih.gov; www.SigmaAldrich.com

[a] Logarithm of acid dissociation constant

[b] Logarithm of the octanol-water partition coefficient

The samples presented a neutral pH (7.01), and the parameters used to characterize wastewater quality like organic matter and suspended solids were evaluated at the WWTP laboratories at the time of collection. Parameters were within the Portuguese legal limits for discharge into water bodies (DL 236/98). An initial screening of the studied contaminants was carried out in the wastewater used in the assays, and all were below the analytical detection limits (0.55 μg L^{-1} of CAF, 0.80 μg $L^{-1}$of MBPh, and 3.3 μg L^{-1} of TCS) (Guedes 2015b).

Plant collection

The exemplars of *S. maritima* were collected in Tagus river estuary (38° 36′ 59.39″ N; 9° 02′ 33.41″ W). This species is abundant in the intertidal and has a wide geographic distribution in temperate zones. This species belongs to a lower zone of a salt marsh having characteristics to a partial or total submergence, high soil salinity, and soil anoxia (Mateos-Naranjo et al. 2010).

S. maritima was collected in May, June, and October 2014. After collection, plants were immediately transported to the laboratory in controlled conditions (refrigerated and avoiding light exposure). The roots were thoroughly washed to remove any sediment particles attached to their surface, submersed (approx. 1 min) in a solution with sodium hypochlorite (0.5%) to stop microbial action, and rinsed with deionized water (approx. 30 s). Experiments were then started.

Experimental design

To simulate CWs, two matrices were used in the experimental assays:

i. Water (W)—aiming to evaluate the removal efficiency in a simpler aquatic medium (deionized water) minimizing matrix interferences
ii. Wastewater (WW)—simulating more realistic conditions

and three main variables were tested for both matrices, W and WW:

(a) LECA (unplanted LECA, L)
(b) *S. maritima* (only plant, P)
(c) *S. maritima* and LECA (planted LECA, PL)

The experimental design of the work is shown in Table 2.

W were operated in a batch mode, i.e., only one PPCP spiking dose at time 0. WW were carried out in fed-batch modes, i.e., PPCPs injected in pulses at specific times. Both systems were carried out under laboratory conditions at room temperature (22 ± 2 °C).

W assays were divided into the following:

W1: Three days to assess L removal efficiency in short periods of time
W2: Seven days to assess L, P, and PL removal efficiency in the hydraulic retention time used for both mesocosm studies and full-scale CWs (Weber and Legge 2011)

Both assays (W1 and W2) were spiked with 0.2 mg of each contaminant and carried out under dark conditions.

WW assays were divided into the following:

W1: Seven days to assess L, P, and PL removal efficiency simulating successive arriving of contaminants (i.e., controlled experimental microcosm spiked every 2 days (0, 2, 4, and 6 days) making the mass of each

Table 2 Experimental design of the work

Assay	Number	Time (days)	PPCPs (mg)	Presence of light	Variables	Code
W	1	3	0.2	No	LECA	W1-L
	2	7	0.2	No	LECA	W2-L
					Plant	W2-P
					Planted LECA	W2-PL
WW	1	7	0.2–0.8[a]	Yes	LECA	WW1-L
					Plant	WW1-P
					Planted LECA	WW1-PL
	2	7 plus 7	0.1–0.3[b]	No	LECA	WW2-L
					Plant	WW2-P
					Planted LECA	WW2-PL

Controls were also carried out with spiked matrices without LECA and *S. maritima* (W#-C and WW#-C)

[a] Flasks were spiked at days 0, 2, and 4 and with 0.2 mg for each time making the mass range from 0.2 to 0.8 mg

[b] Flasks were spiked at days 0, 3, and 6 (first cycle) and 7, 10, and 13 (second cycle) making the mass range from 0.1 to 0.3 mg for each cycle

contaminant ranges between 0.2 and 0.8 mg). The higher mass of contaminants aimed to assess the mobilization and/or contaminants removal testing harsh field conditions. This assay was carried out under sunlight exposure aiming to assess PPCP photodegradation.

W2: Seven days to assess L, P, and PL removal efficiency simulating successive arriving of contaminants (i.e., controlled experimental microcosm spiked every 3 days (0, 3, and 6) making the mass ranges between 0.1 and 0.3 mg) followed by effluent drainage and refill with fresh effluent for the second 7-day cycle following the same spiking scheme. Contaminants' concentration was decreased to values more similar to those reported in the WWTP (Heberer 2002). This assay was carried out in dark conditions at the substrate level to simulate real light field conditions. From the three contaminants previously tested, only the two with lower removal efficiency observed in WW1 (CAF and MBPh) were used aiming to improve system removal efficiency.

Controls were also carried out to a test:

i. The self-capacity of the system to decrease PPCP levels—only spiked matrix (deionized water, W#-C, and wastewater, WW#-C)
ii. Plants vitality (CV) in the systems—plants in non-spiked matrix with LECA (CV_{LECA}) and without LECA ($CV_{w/o\ LECA}$)

General procedure The experiments were carried out in glass flasks (Erlenmeyer's 500 mL). The setups were prepared with 100 g of dried LECA and 200 mL of the liquid matrix corresponding a liquid/solid ratio of 2 followed by spiking with the concentration mentioned above. Water level was maintained above the LECA surface. The setups were not refilled during the assays as the loss of water was considered negligible (RSD = 6%).

S. maritima with similar biomass and height were divided into groups to achieve a total plant weight of 8.0 ± 1.0 g. At the end of the assays, plants were weighted, and compared to the initial value, no biomass differences were observed.

The W1 and W2 were carried out in May. The WW1 was carried out in June and the WW2 in October. The applied treatments were compared in each assay but not between assays. Assays were carried out in duplicate.

Analytical methodologies

Liquid samples were filtered through 0.45-μm nylon filters (diameter 47 mm) from Filter-Lab (Barcelona, Spain), acidified to pH 2 using nitric acid (1:1 *v*/*v*) and extracted by solid-phase extraction (SPE) using Oasis HLB columns (200 mg, 6 mL) from Waters Corporation (Millford, MA, USA). The cartridges were conditioned with MeOH, followed by re-equilibrium with Milli-Q water before sample loading. Analyte recovery was performed by elution with 2 × 3 mL of MeOH. Whenever needed, the samples were concentrated under a gentle stream of nitrogen. Qualitative and quantitative analyses were performed using a high-performance liquid chromatographer (HPLC; Finnigan MAT HPLC system from Thermo Scientific, USA) equipped with a SP P4000 Pump, an AS 3000 Autosampler, a diode array detector (DAD; TSP Spectra SYSTEM UV6000LP), and a TSP SN 4000 Interface. The wavelength was set between 200 and 800 nm. The chromatographic conditions were adapted from Guedes et al. (2015a). The recovery for the aqueous samples ranged between 80 and 120%. The removal of each contaminant was considered the difference between the mass added during the whole assay (m_i) and the mass remaining at the end of the assay (m_f). The removal efficiency was calculated according the Eq. (1).

$$\text{Removal efficiency} = \frac{(m_i - m_f)}{m_i} \times 100$$

The chlorophylls *a* and *b* and carotenoid contents of plants were determinated according to the procedure of Lichtenthaler and Wellburn (1983). Briefly, leaves were cut in small pieces (0.20 ± 0.06 g) and put in glass tubes in a solution of 80% of ACE (10 mL) in darkness. Tubes were manually agitated twice per day. After 48 h, the target wavelengths were read on a spectrophotometer (UV-Visible Thermo Spectronic Helios Gamma).

Statistical analysis

Statistically significant differences among samples for 5% level of significance were evaluated through ANOVA tests using Graph-Pad Prism software and Tukey pairwise comparisons.

Results

pH

Table 3 shows pH values at the end of the assays.

In the W assays, the pH significantly increased ($p < 0.05$) in the presence of LECA (10.55 for W1-L and 10.70 for W2-L) and planted LECA (9.80 for W2-PL) compared to the 5.50 observed for the deionized water control (W-C). In the presence of plant (W2-P), the pH slightly increased and was not significantly higher ($p > 0.05$) than that in the control (W2-C).

Table 3 pH values for W and WW assays (mean ± SD, $n = 2$). *Different letters* represent statistical significant differences ($p < 0.05$)

	Code	3 days (W1)	7 days (W2)	7 days (WW1)	7 days (WW2)	14 days (WW2)
Treatments	L	10.5 ± 0.1^{a}	10.7 ± 0.3^{a}	9.6 ± 0.1^{a}	9.7 ± 0.2^{a}	9.9 ± 0.0^{a}
	P	–	6.0 ± 0.3^{b}	7.1 ± 0.1^{b}	7.1 ± 0.1^{b}	7.5 ± 0.2^{b}
	PL	–	9.8 ± 0.2^{a}	8.3 ± 0.2^{a}	8.5 ± 0.1^{a}	8.7 ± 0.2^{a}
Controls	W-C	5.5 ± 0.0^{b}	5.5 ± 0.0^{b}	–	–	–
	WW-C	–	–	7.4 ± 0.1^{b}	7.5 ± 0.1^{b}	7.9 ± 0.0^{b}
	$CV_{w/o\ LECA}$	–	5.6 ± 0.3^{b}	6.7 ± 0.2^{b}	7.1 ± 0.0^{b}	7.3 ± 0.0^{b}
	CV_{LECA}	–	8.8 ± 0.2^{a}	8.3 ± 0.1^{a}	8.2 ± 0.3^{a}	9.1 ± 0.0^{a}

In the WW assays, the same pH tendency was observed. Compared with the wastewater control (WW-C, 7.4–7.9), LECA (WW1-L and WW2-L) significantly increased the pH to 9.6–9.9 and planted LECA beds (WW1-PL and WW2-PL) to 8.3–8.7. The presence of plant (WW1-P and WW2-P) did not promote pH variations.

Plant vitality

Plants in W1, W2, and WW1 showed no visual signs of stress symptoms in comparison with controls of plant vitality. In WW2 assay, the photosynthetic pigments (chlorophyll *a* and *b*, total chlorophyll, and carotenoids content) of plant leaves were determined as a measure of possible stress induced by the presence of contaminants (Fig. 1). No statistical differences ($p > 0.05$) were observed between plants exposed (microcosms) or not exposed (control vitality) to the PPCPs in the tested concentration.

PPCP removal

Simple aquatic media assays—W#

Figure 2 shows the removal efficiencies of contaminants at the end of the W assays.

In 3 days, W1-L removed around 45% of CAF and TCS and 68% of MBPh. The removal was higher in 7 than in 3 days being statistically different ($p < 0.05$) for TCS with a removal up to 80%.

Compared with LECA, *S. maritima* removal of CAF and MBPh was 35 and 12% respectively lower ($p < 0.05$) than that of W2-L. TCS removal was enhanced by 13% ($p < 0.05$) in the presence of *S. maritima* (removal of 93%).

The planted LECA beds (W2-PL) presented removal efficiencies similar ($p > 0.05$) to the unplanted beds (W2-L) for the three contaminants.

Wastewater assays—WW#

The removal rates in the presence of wastewater (WW assays) were higher than those in the presence of deionized water (W assays). Table 4 shows removal efficiencies (%) for each contaminant at the end of WW assays.

For the assay running for 7 days (WW1), CAF was less removed by plant (WW1-P) than by LECA (WW1-L) (44 vs. 83%; $p < 0.05$) in contrast with MBPh (64 vs. 58%; $p < 0.05$) and TCS (93 vs. 88%; $p > 0.05$). The planted beds (WW1-PL) significantly increased (between 20 and 30%; $p < 0.05$) CAF removal compared to the isolated treatments (WW1-L and WW1-P). Compared with the control, all the treatments, LECA (L), *S. maritima* (P), and planted LECA beds (PL), presented identical removals ($p > 0.05$). The only exception was found for higher CAF removal by LECA (83%) than the control (by 54%).

For WW2, assay running in sequence (7 + 7 days) and after the first period of 7 days, compared with the control (WW2-C), unplanted LECA beds (L) showed lower CAF removal (54%; $p < 0.05$) but increased MBPh removal (97%; $p > 0.05$), whereas the presence of plant (P) and planted LECA beds (PL) provided a similar CAF removal (approx. 80%; $p > 0.05$) and a slight increase (10%; $p < 0.05$) in MBPh removal. Comparing the isolated treatments (L and P) with planted LECA beds (PL), CAF was significantly less removed in L (54 vs. 81%; $p < 0.05$), whereas MBPh had a similar removal between treatments (97%; $p > 0.05$). After the second period of 7 days, there was a similar trend as the one observed for the first 7 days, except for the two following cases. In the control (WW2-C), CAF was 10% less removed than MBPh and similar MBPh removal was observed between the control (WW2-C) and LECA (WW2-L).

Discussion

The pH increase in the presence of LECA is mainly associated with LECA properties, as already reported in literature (Dordio and Carvalho 2013). This pH increase resulted in a pH higher than the pKa of contaminants (see Table 1), except for CAF (pKa = 14), suggesting that contaminants should be in an ionized form in the solution (either in water or wastewater), which may have influenced contaminant removal rates.

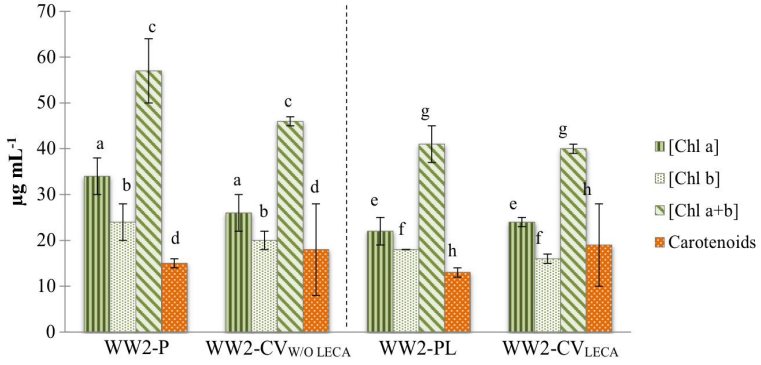


Fig. 1 Content of chlorophylls (*a*, *b*, total chlorophyll) and carotenoids (mean ± SD, $n = 2$) at the end of the assay of *S. maritima*. *Different letters* indicate statistically significant differences ($p < 0.05$) between treatments (*WW2-P* and *WW2-PL*) when compared to the respective control ($CV_{w/o\ LECA}$ and CV_{LECA})

Comparing deionized water with wastewater, the contaminant removals increased when wastewater was used. Therefore, the possible presence of microbiological populations in the used wastewater may explain this increased removal (Cydzik-Kwiatkowska and Zielińska 2016) as the studied compounds have been reported as biodegradable (Gago-Ferrero et al. 2012; Matamoros et al. 2012; Zhang et al. 2013b; Matamoros et al. 2015). TCS photodegradation can also be an important removal mechanism in the experiment under sunlight exposure (Matamoros et al. 2012; Zhang et al. 2013a; Vione et al. 2013). Although with a slightly higher removal percentage, the concentration of each target PPCP removed is similar in wastewater with and without sunlight exposure.

The potential of LECA to promote contaminant removal was less pronounced in wastewater than in deionized water. The presence of LECA promoted PPCP removal in deionized water, specially MBPh and TCS through a sorption process, which are being largely dependent on the lipophilicity of the compounds (Luo et al. 2014). The higher removals of MBPh and TCS, compared to CAF, may be explained by their octanol-water partition coefficient (Log $K_{ow} > 3$) and solubility (Table 1), which promote their retention by adsorption to the surface of the solid matrix. Higher residence times increased contaminant removal, as observed in other works (Matamoros et al. 2015), but the highest removal rate was observed in the first 3 days of experiment (see Fig. 2), namely for CAF and MBPh.

The species of plant *S. maritima* showed no stress symptoms even when exposed to the higher PPCP concentration. In the tested conditions, *S. maritima* showed a general tendency to promote higher removal of lipophilic than hydrophilic contaminants: TCS > MBPh > CAF. Phytoremediation processes that could contribute to the contaminant decrease are (i) uptake as recent studies increased the range of contaminant uptake (Zhang et al. 2013a; Carter et al. 2014; Wu et al. 2015), (ii) adsorption to plant roots, namely lipophilic contaminants, and

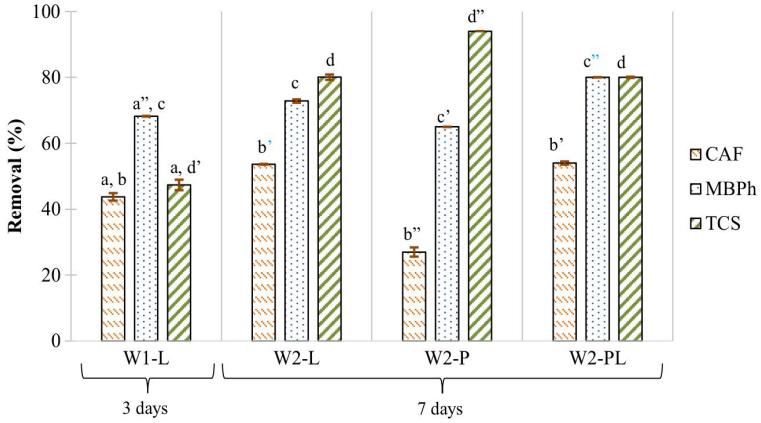


Fig. 2 Rate of contaminants removed in simple aquatic media (W assays): after 3 days with LECA (*W1-L*) and after 7 days with unplanted LECA (*W2-L*), *S. maritima* (*W2-P*), and planted LECA (*W2-PL*) (mean ± SD, $n = 2$). *Different symbols* (*x*, *x'*, *x"*) indicate statistical differences ($p < 0.05$). *Letter a* indicates statistic differences for W1-L treatment between CAF, MBPh, and TCS. *Letter b* indicates statistic differences for CAF between the different variables (L, P, and PL). *Letter c* indicates statistic differences for MBPh between the different variables (L, P, and PL). *Letter d* indicates statistic differences for TCS between the different variables (L, P, and PL)

Table 4 Removal efficiencies (%) for CAF, MBPh, and TCS at the end of the WW1 and WW2 (mean ± SD, $n = 2$). *Upper* and *lowercase* (*x*, *X*, *X'*) *letters* represent statistical significant differences ($p < 0.05$)

	Control (C)			LECA (L)			Plant (P)			Planted LECA (PL)		
	WW1	WW2		WW1	WW2		WW1	WW2		WW1	WW2	
	7 days	1st cycle (7 days)	2nd cycle (7 days)	7 days	1st cycle (7 days)	2nd cycle (7 days)	7 days	1st cycle (7 days)	2nd cycle (7 days)	7 days	1st cycle (7 days)	2nd cycle (7 days)
CAF	$54 \pm 10^{a, C}$	$89 \pm 3^{d, e, g}$	$79 \pm 4^{d, e}$	$83 \pm 1^{A, c}$	$54 \pm 0^{D, e, g}$	$65 \pm 6^{d, E}$	$44 \pm 6^{a, C}$	$83 \pm 0^{d, e, g}$	$84 \pm 1^{d, e}$	$77 \pm 1^{A, C}$	$81 \pm 2^{d, e, g}$	$85 \pm 3^{d, e}$
MBPh	$61 \pm 11^{b, C}$	$85 \pm 2^{e, G}$	89 ± 1^{e}	$58 \pm 1^{b, C}$	$97 \pm 1^{e, G}$	91 ± 0^{e}	$64 \pm 3^{b, C}$	$96 \pm 0^{e, G}$	$>97^{e}$	$65 \pm 6^{b, C}$	$97 \pm 0^{e, G}$	$>97^{e}$
TCS	$85 \pm 7^{c, f}$	–	–	$88 \pm 5^{c, f}$	–	–	$93 \pm 1^{c, f}$	–	–	91 ± 2^{c}	–	–

WW1 run for 7 days [treatments were spiked every 2 days making the concentrations range from 0.2 to 0.8 mg]. WW2 run for 14 days [treatments were spiked every 3 days (days 0, 3, 6 (first cycle) and 7, 10, and 13 (second cycle)) making the concentrations range from 0.1 to 0.3 mg]

[a] CAF: WW1-PL with other WW1 treatments (percentage statistically significantly different at $p < 0.05$)

[b] MBPh: WW1-L with other WW1 treatments (percentage statistically significantly different at $p < 0.05$)

[c] Between contaminants (CAF, MBPh, and TCS) for WW1 (percentage statistically significantly different at $p < 0.05$)

[d] CAF: WW2-L with other WW2 treatments (percentage statistically significantly different at $p < 0.05$)

[e] Between first cycle and second cycle in WW2 for each contaminant (CAF and MBPh) (percentage statistically significantly different at $p < 0.05$)

[f] TCS: WW1 between the different treatments (percentage statistically significantly different at $p < 0.05$)

[g] Between contaminants (CAF, MBPh, and TCS) for WW2 (first cycle, 7 days) (percentage statistically significantly different at $p < 0.05$)

(iii) rhizoremediation as, e.g., the root can provide a surface area for attached microbial growth (Hijosa-Valsero et al. 2011).

This suggests that LECA and *S. maritima* can be an option to decrease PPCP levels, but further work would enlarge the application range in CWs by (i) using more recalcitrant compounds and (ii) enlarging the system to several cycles in the light of real system applications that are built to work for 20 years.

Conclusions

In the tested conditions, the different components of CWs showed the capacity to promote PPCP removal between 19 and 93% in deionized water and 44 and 97% in wastewater.

Higher removal (around 61–97%) was observed for the lipophilic compounds (MBPh and TCS) compared with the hydrophilic one (CAF; around 19–85%), which is attributed to their physicochemical characteristics thus influencing responses in the presence of LECA and/or *S. maritima*.

The removal pattern showed to be similar between successive cycles suggesting that system components have potential to remove PPCPs in a continuous way.

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PAPER II *Influence of the cell design in the electroremoval of PPCPs from soil slurry*

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Influence of the cell design in the electroremoval of PPCPs from soil slurry

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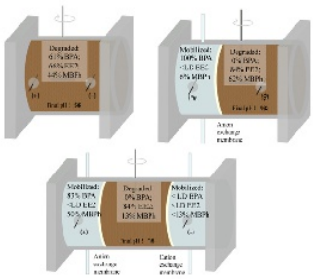
HIGHLIGHTS

- In 72 h, the EK/ED process showed to be a promising technology for PPCPs removal from soil slurry.
- Contaminants were removed from soil slurry between 44% and 100%.
- Cell design influences the PPCPs removal.
- Electric current shows effect in contaminants removal (degradation and/or mobilization) between 9% and 84%.

GRAPHICAL ABSTRACT



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ABSTRACT

The effluent from wastewater treatment plants (WWTPs) have been extensively reused for various purposes in many regions of the world, including landscape and agricultural irrigation. However, the elimination of pharmaceuticals and personal care products (PPCPs) in conventional WWTPs is not complete and consequently they may be present in effluent which, can be used for soil irrigation. This work discusses the efficiency of electro based processes, applied to soil slurry aiming PPCPs removal. Three different cell designs were tested, with three-, two- and one-compartment(s) (3C-, 2C- and 1C-cell, respectively). In the case of the 3C- and 2C-cells, ion exchange membranes were used for compartment division. Three PPCPs with different physical and chemical characteristics were studied: bisphenol A (BPA), 17α-ethinyloestradiol (EE2) and oxybenzone (MBPh). All experiments were carried out for 3 days with a current density of 0.02 mA cm^{-2}. After the electro based experiments, 44%–100% of the three contaminants were removed (mobilized and/or degraded) from the soil slurry. The highest removal rates (>83%) were achieved for BPA and EE2. BPA and MBPh were mainly mobilized towards an anode compartment, whereas EE2 was mainly degraded. Among all the tested cell designs, 1C-cell showed a broader range to contaminants removal from soil through electrodegradation. The 1C-cell also presents the main advantage of degrading the PPCPs of removing and accumulating them in another compartment, where degradation might not occur.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are one class of contaminants that have not yet been regulated and are continually introduced into the environment through different anthropogenic sources. One of the PPCPs main sources is the wastewater treatment plants (WWTPs) as, in many cases, they are unable to efficiently remove these compounds [1,2]. In order to reduce the demand on water supplies, the effluent from WWTPs have been extensively reused for various purposes in many regions of the world, including landscape and agricultural irrigation [3].

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However, this can be a real problem as PPCPs can accumulate in soils [4], potentially contaminating groundwater [5] and surface water [6,7] or enter the food chain [3,8,9]. Few studies reported that PPCPs were detected in plants grown in soils submitted to biosolids application and irrigated with effluent. Malchi et al. (2014) [10] found 14 different PPCPs, such as carbamazepine, caffeine, clofibric acid, diclofenac, ibuprofen, ketoprofen and naproxen in carrots and sweet potatoes irrigated with treated wastewater. Calderón-Preciado et al. (2011) [2] also reported the occurrence of a wide range of PPCPs e.g. salicylic acid, caffeine, ibuprofen, methyl dihydrojasmonate and galaxolide, in apple tree leafs and alfalfa with concentrations of 0.016–16.9 ng g^{-1} (wet weight). Wu et al. (2015) [9] detected caffeine, carbamazepine, naproxen and triclosan in eight vegetables, with a total PPCPs concentration in the range of 0.01–3.87 ng g^{-1} (dry weight). The health disorders most frequently associated with the exposure to these contaminants mainly include the development of resistance to pathogens and endocrine disruption, even at very low concentrations [11,12].

The electrokinetic (EK) process is a remediation technique that uses a low level direct current (DC) as the "cleaning agent". EK based technologies have already demonstrated to have potential to remove different types of contaminants from several contaminated matrices alone and/or coupled with other technologies [13–17]. In the electrodialytic (ED) process, ion-exchange membranes are used to separate the matrix from the solutions in the electrode compartments [18]. The ED process was developed at the Technical University of Denmark in 1992, patented in 1995 (PCT/DK95/00209), and has proven to be a faster process to be used ex situ for the removal of heavy metals [19], polycyclic aromatic hydrocarbons [20] and polychlorinated biphenyls [21] from soil slurry. In order to improve the process different studies have been carried out, e.g. Ottosen et al. (2012) [22] showed a faster remediation of heavy metals in a stirred ED system instead of a stationary one. With PPCPs, one recent study [14] tested the applicability of the EK process for the removal of 17β-estradiol (E2), 17α-ethinyloestradiol (EE2), bisphenol A (BPA), nonylphenol (NP), octylphenol (OP) and triclosan (TCS) from soil in a stationary laboratory cell. The results showed that EK is a viable method for the PPCPs remediation, through mobilization by electroosmosis and electrodegradation. Still, to the best of our knowledge, no works have been published regarding PPCPs removal from soil slurry using EK/ED technologies.

In this study, the EK and ED processes were applied to contaminated soil suspended in water testing different cell designs: two ED cells (with 3 and 2 cell compartments; 3C- and 2C-cell, respectively), one EK cell, 1 cell compartment (1C-cell), and their controls (without electric current). Three PPCPs were studied: bisphenol A (BPA), 17α-ethinyloestradiol (EE2) and oxybenzone (MBPh), as they present different physical and chemical characteristics (Table SM1) and were already detected in various environmental compartments [4,23–25]. This study aims to find a remediation solution for PPCPs associated with effluent irrigation in agricultural soils.

2. Materials and methods

2.1. Standards and chemicals

BPA (P99%), EE2 (P98%) were purchased Sigma–Aldrich (Steinheim, Germany) and MBPh (P98%) from Alfa Aesar (U.S.A.). Methanol (MeOH), acetonitrile (ACN) and acetone (ACE) were HPLC grade from Riedel-de Haën (Germany). Acetic acid (LC–MS grade), sodium hydroxide (NaOH) were purchased from Sigma–Aldrich. Formic acid (LC–MS grade) was from Fluka and sodium nitrate ($NaNO_3$) was reagent grade from Panreac. Deionized and Mili-Q water (Mili-Q plus from Milipore; Bedford, MA, USA) were used whenever needed.

2.2. Soil sampling and characterization

The soil was sampled from Paul de Magos, Salvaterra de Magos, Portugal, at 0–20 cm depth, corresponds to a Fluvisol (World Reference Base for Soil), and its characteristics are presented in Table 1. The soil has a silty loam texture (with 53.4% clay), high mineral and organic colloid contents, which leads to a high cation exchange capacity. The soil was spiked with 3 mg L^{-1} of each contaminant in 1:1 MeOH:ACE.

2.3. Experimental setup

The experiments were carried out in duplicate (n = 2), for 3 days (72 h) with a constant current density of 0.02 mA cm^{-2}, according to the conditions presented in Table 2. Three different cell designs were tested (Fig. 1a–c). Control experiments (with no applied current) were also carried out for all cell designs. All the experiments were conducted in the laboratory under controlled temperature (22 °C).

The experiments were carried out in cylindrical Plexiglas-cells, with an internal diameter of 8 cm. The compartment where the soil was placed had a L = 10 cm and was equipped with a stirrer, whereas the electrolyte compartments had a L = 5 cm. The electrodes were platinized titanium bars, with a 3 mm diameter and a 5 cm length (Bergsøe Anti Corrosion A/S, Herfoelge, Denmark). A power supply (Agilent E3612A) was used to maintain a constant current. The ion-exchange membranes used were commercial ones from Ionics (anion exchange membrane, AEM: AR204 SZRA B02249, and cation exchange membrane, CEM: CR67 HUY N12116B). In all treatments, the soil was kept suspended in deionized water, with a liquid-to-solid ratio (L/S) of 5 (75 g of soil in 375 mL of deionized water), due to continuous stirring (RW11 basic from IKA). The electrolyte was a 10^{-2} M $NaNO_3$ solution (500 mL) without pH adjustment, being circulated, 4 mL min^{-1} in a closed system, by means of a peristaltic pump (Watson-Marlow 503 U/R, Watson-Marlow Pumps Group, Falmouth, Cornwall, UK). Conductivity and pH in the soil slurry, and the voltage between working electrodes were measured twice a day in all experiments.

In the 3C-cell the electrode compartments were separated from the soil compartment (central compartment) by an AEM and a CEM (Fig. 1a). In the 2C-cell the electrode compartment was separated from the soil compartment (cathode compartment, 2C-CAT) by an AEM (Fig. 1b). In the 1C-cell (Fig. 1c) the only compartment contained the soil slurry (electrolyte and membranes were not used).

Table 1
Characteristics of the soil used in the experiments.

Parameters	Value
Sand (%)	19.7
Silt (%)	26.9
Clay (%)	53.4
$pH_{(H2O)}$	5.8
Total carbon (g kg^{-1})	24.6
Organic content (g kg^{-1})	42.4
Cation exchange capacity ($cmol_{(+)}$ kg^{-1})	22.7
Exchangable cations ($cmol_{(+)}$ kg^{-1})	
Ca^{2+}	11.3
Mg^{2+}	5.7
K^{+}	0.5
Na^{+}	1.2
Sum of exchangable cations ($cmol_{(+)}$ kg^{-1})	18.7

Table 2
Experimental conditions.

Experiment	Soil slurry compartment	L/S[4]	Membrane	Current density (mA cm^{-2})	Time (day)	Scheme figure
3C[1]	Central	5	AEM[5]/CEM[6]	0.02	3	1a)
2C[2]	Cathode	5	AEM	0.02	3	1b)
1C[3]	Only one	5	–	0.02	3	1c)
Control-3C	Central	5	AEM/CEM	–	3	1a)
Control-2C	Cathode	5	AEM	–	3	1b)
Control-1C	Only one	5	–	–	3	1c)

[1] 3C = 3 compartments cell: anode, central and cathode.
[2] 2C = 2 compartments cell: anode and cathode.
[3] 1C = 1 compartment cell, where the pair of electrodes were introduced.
[4] L/S: liquid-to-solid ratio.
[5] AEM: anion exchange membrane.
[6] CEM: cation exchange membrane.

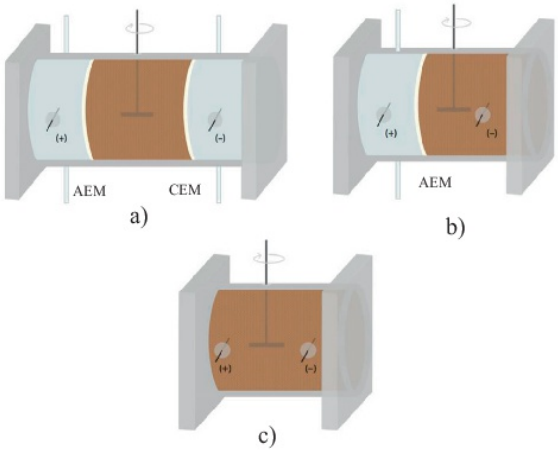

Fig. 1. Schematic representation of the laboratory cells used in the experiments: a) 3C-cell, b) 2C-cell, c) 1C-cell. The separation between the soil slurry and the electrode compartments was made through ion exchange membranes (AEM and/or CEM).

2.4. Sample preparation

By the end of the experiments, the soil slurry was filtered under vacuum and separated in liquid (water) and solid phase (soil). The liquid phase was filtered through MFV-5 glass microfiber filters (diameter 47 mm, pore size 0.5 μm) from Filter-Lab (Barcelona, Spain) and then extracted (Section 2.4.2). The filtrated soil was also extracted for PPCPs determination as described below (Section 2.4.1), and the remaining soil was dried in an oven at 50 °C till constant weight and the water content determined.

2.4.1. Soil samples extraction

The soil was extracted (n = 3) following a QuEChERS adapted from [26]. Extract tubes were obtained from Waters (Dublin, Ireland). The acetate buffer contained 1.5 g NaOAc and 6 g $MgSO_4$. The dispersive phase contained 150 mg PSA (primary and secondary amine) and 900 mg $MgSO_4$. A 5 g of homogenized soil was weighed in a 50 mL polypropylene centrifuge tube with 3 mL of purified water (pH of 2.50 adjusted with HCl) and manually shaken. Then, NaOAc and $MgSO_4$ was added and swirled on a vortex mixer for 4 min with higher speed, following 4 min in an ultrasonic bath. After that, 7 mL of acetonitrile (1% HCOOH) was added, agitated in a vortex (4 min) and placed in an ultrasonic bath for 4 min. Then, the extract was centrifuged at 4000 rpm for 10 min. An aliquot of the supernatant (acetonitrile phase) was transferred to a 15 mL centrifuge tube containing the PSA and $MgSO_4$, and was manually shaken for 10 s and swirled on a vortex mixer for 60 s. After this step, the extract was centrifuged again (4000 rpm for 10 min), and 4 mL supernatant were transferred to a glass vial. The extract was evaporated under a gentle stream of nitrogen till 0.5–1 mL. All samples were stored at −18 °C until analysis.

2.4.2. Liquid samples extraction

The extraction of the analytes, present in the electrolyte solutions and in the water from the soil filtration, was performed by solid phase extraction (SPE), using Oasis HLB (200 mg, 6 mL) cartridges, from Waters Corporation (Millford, MA, USA). For PPCPs enrichment, the samples were acidified to pH 2 using nitric acid (1:1 v/v) before extraction. The SPE cartridges were conditioned with 2 × 3 mL of MeOH, followed by 2 × 3 mL of Milli-Q water. Afterwards, the aqueous samples (200 mL) were passed through the cartridge at a flow-rate of ≈10 mL min^{-1} by applying a moderate vacuum. The cartridges were vacuum dried for ≈1 min. The retained analytes were eluted sequentially with 2 × 3 mL of MeOH for HPLC analysis. The sample extracts were concentrated to 0.5–1 mL under a gentle stream of nitrogen and later analyzed. All samples were stored at −18 °C until analysis.

2.5. PPCPs analysis

Quantitative analysis was performed by high-performance liquid chromatography (HPLC; Finnigan MAT HPLC system from Thermo Scientific, USA) equipped with a SP P4000 Pump, an AS 3000 autosampler and a diode array detector (DAD; TSP Spectra SYSTEM UV6000LP). The wavelength was set between 200 nm and 800 nm and a TSP SN 4000.

The analytes separation was carried out using Chromolith HighResolution RP-18e column with 100 mm × 4.6 mm from VWR (Darmstadt, Germany) and Onyx SecurityGuard C18 cartridges (5 × 4.6 mm) from Phenomenex (Torrance, USA).

All HPLC runs were performed at a constant flow rate of 1 mL min^{-1}, in gradient mode. The eluents used were acetonitrile/MiliQ water solutions (solution A: 35/65; solution B: 90/10). The chromatographic conditions were adapted from Guedes et al. (2015) [27]. The limit of detection (LD) and quantification (LQ) of each contaminant can be consulted in Supplementary material (Table SM2).

2.6. Statistical analysis

Statistically significant differences among samples for 5% level of significance were evaluated through ANOVA tests using Graph-Pad Prism software and Tukey pairwise comparisons.

3. Results and discussion

3.1. General results

In order to follow EK/ED process parameters: conductivity (Fig. 2), voltage (Fig. 3) and pH (Fig. 4) were measured along the experiments.

In the 1C-cell the conductivity remained constant during the experiment meaning that no depletion of ions was verified. The slurry soil conductivity in 3C- and 2C-cell decreased 8 and 4 times, respectively, within the first 8 h. This represents a quick depletion of free ions from the solution towards the electrode compartment (s), where the conductivity increased. In the 2C-cell, the soil slurry had the highest final conductivity (3 times more; 2C *vs.* 3C-cell; 0.17 mS cm^{-1} *vs.* 0.06 mS cm^{-1}). This may be explained by the 2C-cell set-up design as only the ions with negative charge are removed from the slurry soil, towards the anode compartment, with all the positive ions remaining in solution.

The conductivity experimental data is in accordance with the voltage behaviour (see Fig. 3). In the experiment with 1C, cell without ion exchange membrane(s), the voltage was constant (≈14 V) during the experimental time as the ions were not being removed from the soil slurry (resistance did not change (1444 Ω)).

For the experiments with electrode compartments separated by ion exchange membrane(s) (2C- and 3C-cell) the voltage was higher at the end of the experiments than in the beginning (10.2 V *vs.* 34.8 V and 11.35 V *vs.* 62.85 V; 2C *vs.* 3C respectively). For both designs, the voltage had a logarithmic shaped growth with a quick rise in the first day, then slightly decreased and remained constant until the end of the experiments.

In 3C-cell design the electrodes were not placed directly into the soil slurry but into an electrolyte solution separated by ion exchange membranes. This resulted in a higher increase of the resistance comparing with 2C-cell (6 times *vs.* 4 times, Table SM3) due to the higher depletion of ions from the soil slurry. The 2C-cell was expected to have lower resistance than the 3C-cell since the set-up only consisting of two compartments separated by AEM, where the electrolysis reaction at the anode results in a higher conductivity of the soil slurry at the end of the experiment (0.17 mS cm^{-1} *vs.* 0.06 mS cm^{-1}; 2C *vs.* 3C-cell). This also results in a lower potential energy (W) between the two electrodes for 2C when comparing with 3C-cell (0.102 to 0.348 W for 2C, and 0.136 to 0.7546 W for 3C).

Concerning pH behaviour (see Fig. 4), the controls (without applied current) showed no differences between the initial and the final pH for soil slurry and electrode compartments (AN and CAT). In the experiments with applied current, the pH decreased

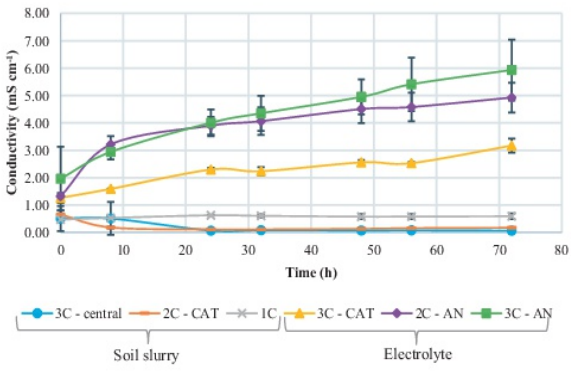

Fig. 2. Conductivity (mS cm^{-1}) variation with time in the different compartments for the three cell designs (3C, 2C and 1C).

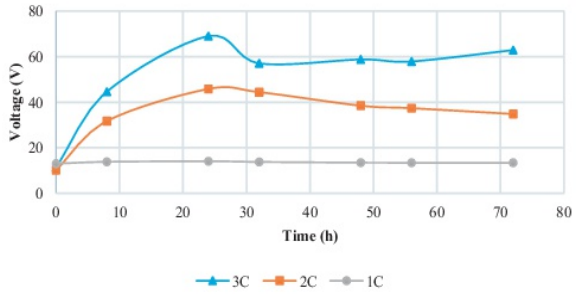

Fig. 3. Variation of voltage with time for the three different designs of cell: 3C, 2C and 1C.

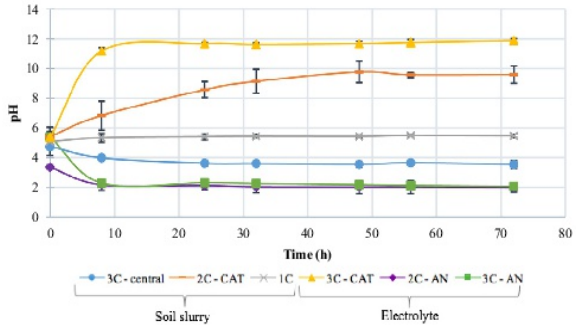

Fig. 4. pH variation with time in the different compartments for the three designs of cell: 3C, 2C and 1C.

over time in the anode compartment (from pH ≈ 5.5 to pH around 2) due to the formation of H^+ and increased (pH > 9) in cathode due to the generation of OH^-.

The soil slurry pH underwent variation in cell compartments comparing 2C-cell with 1C- and 3C-cell:

- For 1C-cell, the soil slurry pH remained the same from the beginning (pH 5.1 ± 0.5) until the end (pH 5.5 ± 0.1) of the experiment indicating a good buffering capacity of the system as the formation of H^+ was overcome by the OH^- generation.
- For 3C-cell the soil slurry (central compartment) slightly decreased (from 4.74 ± 0.61 to 3.55 ± 0.26), which is explained by the passage of H^+ from the anode compartment to the central compartment through the AEM, as well as due to the water splitting at the AEM in the central compartment.
- In the 2C-cell, the soil slurry pH increased till 9.60, which is higher than the pKa of the PPCPs under study. This means that the three contaminants were in their ionized forms contrary to the other cells designs. It should be noted that the slightly lower pH in the cathode compartment of the 2C experiment, comparing to the 3C, might be explained by the electromigration of some OH^- ions towards the anode compartment, as well as due to the soil buffering capacity.

3.2. PPCPs removal

At the end of all experiments, the difference between the amount of contaminants detected in the cell (through mass balance calculations) and their initial amount, were expressed as the percentage of contaminant removed by degradation and/or mobilization (through electromigration) to the electrode compartment(s). The percentage of contaminants BPA, EE2 and MBPh

present, in the different compartments of the cell designs, at the end of the experiments is presented in Table 3.

Compound volatilization is not expected to be an important fate process based upon the estimated Henry's Law constant of the here studied compounds (Table SM1). Photodegradation of the compounds is also not expected to occur, once all the experiments were protected from sunlight.

The influence of the current on PPCPs removal was extrapolated through the comparison between the percentage of PPCPs present in the cell with and without electric current (controls).

The experimental results from control set-ups, without applied current, showed differences among contaminants removals (ranging from 23% to 61%; see Table 3) in the slurry soil compartment with PPCPs not being detected in electrode compartment. These removals may be attributed to biotic and abiotic processes that may have occurred along the 3 days of experiments, although no biological analysis were carried out in this study. Guedes et al. (2015) [27] reported a similar result using sewage sludge in a 2C-cell set-up for BPA, EE2 and MBPh. The authors attributed the compounds degradation in controls to bioremediation mechanisms as biological activity was observed in the final collected samples. This hypothesis is supported by previous studies which have shown that degradation of PPCPs in soils is due to microbial activities [28,29]. Additionally, comparative experiments conducted in sterilized soils carried out by Yu et al. (2013) [18] showed that the sterilization treatment resulted in a decrease of the degradation rates of PPCPs e.g. $t_{1/2}$ of BPA increased for sterilized soils, indicating that microbial activity played an important role in BPA degradation. It should be noted that degradation behaviours of PPCPs differed with type of soils, as different soils have different physicochemical properties, microbial populations and activities [18].

The application of a low level DC improved contaminants removal (through electro-mobilization and/or -degradation) in all cell designs, ranging from 9% for BPA to 84% for MBPh, when compared to their controls (see Fig. 5). Concerning the different cell designs, the effect of electric current showed to be similar for 3C- and 2C-cell on PPCPs removal: BPA (≈84%) > EE2 (≈35%) > MBPh (≈10%). In the 1C-cell the current improved PPCPs removal by >60% for BPA and EE2, and by 20% for MBPh. These findings support that the absence of cell compartments is favourable to EE2 and MBPh removal from the soil slurry, possibly through contaminants desorption from the soil to the liquid phase followed by electro-chemical degradation (electrodegradation). The homogenous degradation of the three contaminants in the 1C-cell, comparing to the other tested cell designs, may be attributed to the presence of both cathode and anode electrodes in the soil slurry compartment, thus promoting both reduction and oxidation reactions. The use of a cell with compartments (3C- and 2C-cells) only increased the removal of BPA (≈20%) through mobilization. MBPh showed the lowest improvement when current was applied (≈10% of difference between with and without current (controls)), for 3C- and 2C-cell designs.

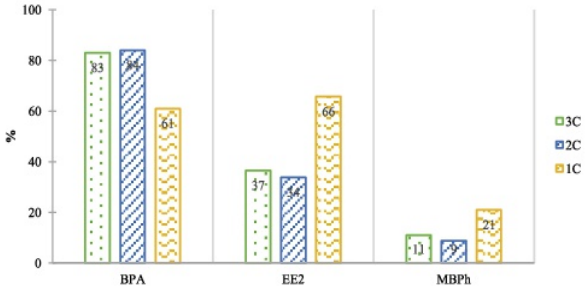

Fig. 5. Difference of contaminant removal (%) in soil slurry by each cell-design (3C, 2C and 1C) between experiments with and without electric current (control).

Overall, the results show that PPCPs removal (amount of contaminant mobilized and/or degraded) is related with the cell design (3C, 2C and 1C) and contaminant type.

After the EK/ED experiments:

- The 3C-cell design presented more than 75% of removal (mobilization + degradation) from soil slurry for the three contaminants. However, although removals are similar in the soil

Table 3
Percentage of contaminant (BPA, EE2 and MBPh) detected in the different cell compartments and degraded, at the end of the experiments in relation to the initial amount (n = 2).

Experiment	Cell-compartment	BPA		EE2		MBPh	
Control-3C	Soil slurry (central)	100	sd	52	sd	36[d]	±17
	Anolyte	<LD	0	<LD	0	3	sd
	Catolyte	<LD	0	<LD	0	<LD	0
	Degradation	0		48	sd	61	±17
3C	Soil slurry (central)	17[a]	±4	16	±9	25[c,d]	±9
	Anolyte	83	±6	<LD	0	50	sd
	Catolyte	<LD	±0	<LD	0	13	sd
	Degradation	0		84	±9	13	±9
Control-2C	Soil slurry (cathode)	100	sd	50[d]	sd	40[d]	±12
	Anolyte	<LD	sd	<LD	sd	2	0
	Degradation	0	sd	50	sd	58	±12
2C	Soil slurry (cathode)	16[a]	sd	16	sd	32[c,d]	±14
	Anolyte	100	±20	<LD	sd	6	±1
	Degradation	0		84	sd	62	±15
Control-1C	Soil slurry	100[b']	±20	100	±20	77[d]	±35
	Degradation	0		0	0	23	35
1C	Soil slurry	39[a,b]	±30	34	sd	56[c',d]	±10
	Degradation	61	±30	66	sd	44	±10

Degradation (%) = [1 − Σ(PPCPs mass detected in all cell compartments)/(PPCPs mass added to soil slurry)] * 100; *<LD: Below detection limit; sd-without standard deviation;* x and x′ mean statistically differences ($p < 0.05$) comparing.

[a] BPA present between cells design (3C, 2C and 1C).
[b] BPA for each cell design and respective control.
[c] MBPh between cells design (3C, 2C and 1C).
[d] MBPh for each cell design and respective control.

slurry, compounds showed different behaviours inside the system. BPA and MBPh were mainly mobilized and thus detected in the anolyte (83% and 50%, respectively), showing low degradation (mainly electro-) rates (0% and 13%, respectively). On the other hand, EE2 suffered 84% of degradation from soil slurry and was not detected in any of the electrolytes.

- The 2C-cell design achieved more than 68% of removal (mobilization + degradation) from soil slurry for the three contaminants. BPA was mainly detected in the anolyte (>80%). EE2 and MBPh presented higher degradation rates (84% and 62%, respectively). The 2C-cell design improved the degradation of MBPh when comparing with 3C-cell (62% *vs.* 13%, $p < 0.05$). This means that when the soil is placed in the cathode compartment MBPh degradation is improved, and when placed in the middle cell compartment it is mobilized to the anode compartment (50%).
- In the 1C-cell design (removal = degradation; no mobilization) the contaminants were removed from soil slurry following the order: EE2 (66%) > BPA (61%) > MBPh (44%). Its experimental results, in opposition to the other tested cell designs, showed to improve the BPA degradation (61%). On the other hand, at the end of the experiments, 39% of BPA was still detected in soil slurry, being higher than in the cell designs 3C (17%) and 2C (16%) ($p > 0.05$). Concerning the amount of contaminants removed from soil slurry, significant statistical differences ($p < 0.05$) were only observed for MBPh between 3C and 2C cells versus 1C-cell. In 1C-cell all the contaminants removed were degraded eliminating the contaminants instead of transfer to another compartment as in 3C and 2C-cell. This support the hypothesis that the absence of separation compartments may improve the degradation of the three contaminants at the same time.

The PPCPs "behavioural differences" may be attributed to the different chemical structures and degradation mechanisms. BPA was mainly mobilized to anode compartment (>83%) in the 3C and 2C-cell with degradation (electro-chemical degradation) only being observed in the 1C-cell (61%). MBPh also showed to be mainly mobilized towards anode (50%), through AEM, in 3C-cell, but higher degradations were obtained in the 2C-cell. EE2 was not detected in electrolytes, but hypothetically it may pass through the AEM and suffer degradation in the anode compartment. EE2 reactivity and mechanisms were previously studied by other authors [30].

The contaminants under study have a similar Log K_{ow}, ranging between 3.32 and 3.82. However, the EE2 has the lowest solubility (11.3 mg L^{-1}) when comparing to with BPA and MBPh (69 and 120 mg L^{-1}, respectively), which influence compounds mobilization, and consequently their degradation rate. The data suggests that water content of the soil may play an important role on the desorption of the compounds and their consequently mobilization. This is attributed to the creation of larger interaction surfaces between soil and PPCPs that increase their dissolution helping to release PPCPs that are bound in soil fraction. In addition, the pH in the presence of soil slurry is easily changed, which showed to be an important parameter in MBPh degradation/removal, as it increases the contaminant solubility. The pH showed to be an important parameter in MBPh degradation/removal, attributed to increased solubility. Ionizable chemicals, depending on their pKa and on the medium pH, are converted to either cations or anions. When pKa > pH compounds the neutral species are predominant. As the pH of the soil slurry compartment in 2C-cell was 9.14 ± 0.81 after 24 h, MBPh was in its ionized form (pKa = 7.6; pKa < $pH_{soil\ slurry}$). This means that MBPh suffered deprotonation becoming more soluble and being able to migrate from the cathode towards the anode compartment through the AEM, where it may suffer anodic oxidation. The faster mobilization of the MBPh in the 2C-cell comparing to the 3C-cell may explain the differences between the amount of MBPh detected in the anode compartment of the 2C-cell (6%) comparing to the 3C-cell (50%): the faster mobilization resulted in a higher residence time in the anode compartment and, consequently, more time to suffer anodic oxidation. This hypothesis is supported by the degradation rates of MBPh at the end of the experiments: 62% in 2C-cell *vs.* 13% in 3C-cell. For BPA the pH effect was also noticeable. In the 2C-cell the BPA pKa ≈ $pH_{soil\ slurry}$ may have contributed to the higher BPA mobilization towards the anode compartment (>10% comparing with the 3C-cell). The effect of pH on compounds removal has been studied by other authors, e.g. Nam et al. (2014) [31] confirmed that PPCPs behaviour vary from compound to compound and are difficult to predict, because their behaviour is often controlled by interactions with specific functional groups or complex pH-dependent speciation. Previous work reported that PPCPs behaviour is also dependent of matrix characteristics (e.g., ionic strength and natural organic matter) [32]. Oh et al. (2016) [33] reported that natural organic matter naturally present in soil can negatively affect the ibuprofen sorption mechanisms due to competition. The distribution of PPCPs between aqueous and solid phase is dependent of sorption mechanisms, which in turn can affect their degradation and mobilization during the ED process. In the present study, it is not expected a very high influence of the organic matter as the organic carbon water partition coefficient for the three PPCPs in study are considered moderate [34]. In addition, the solubility of PPCPs can also be influenced by the ionic strength. The ionic strength may lower the solubility of neutral compounds but it also induces the dissolution of ionizable acidic compound [35]. Chen et al. [36] examined the effects of ionic strength on the retention and transport of two antibiotics and reported an important role of the ionic strength in controlling the transport of only one of the antibiotics under specific pH conditions. The here obtained results showed that the 1C-cell can be a better option to PPCPs removal by degradation, since this design shows to have a broader contaminant application range for PPCPs with different physical and chemical characteristics.

4. Conclusions

The presence of PPCPs in the environment is more concerning considering that they do not appear individually, but as a complex mixture, which complicates their removal. The EK/ED showed to be a promising technology to remove PPCPs from soil slurry with 44% to 100% of removal (through mobilization and/or degradation) after 72 h, for the three PPCPs in study. The cell design showed to have influence in PPCPs removal. Using cells with divided compartments (3C or 2C), BPA and MBPh were mainly mobilized towards the anode compartment through the action of an electric field, whereas EE2 suffered degradation. However, when soil slurry was placed in the cathode compartment (2C-cell design) degradation of MBPh overcomes its mobilization, which can be explained by pH changes ($pH_{soil\ slurry} > pKa_{MBPh}$). The use of a cell without compartments (1C-cell) showed to be the best option for homogeneous degradation rates of the contaminants under study. Experimental data suggests that 1C cell design may have broader application range for contaminants with different physical and chemical characteristics. Its main advantage showed to be the PPCPs removal by degradation (>44%) instead of their mobilization to electrode compartment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2017.05.148.

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PAPER III *Electrodialytic 2-compartment cells for emerging organic contaminants removal from effluent*

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Electrodialytic 2-compartment cells for emerging organic contaminants removal from effluent

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ABSTRACT

The present work discusses the efficiency of the electrodialytic (ED) process to remove emerging organic contaminants (EOCs) from effluent. The ED process was carried out in a cell of two-compartments (2 C-cell) with effluent in either the anode or cathode compartment, separated from the electrolyte compartment through an anion or a cation exchange membrane (AEM and CEM, respectively). As effluent destination might be soil irrigation, and having in mind the nutrient recycling, phosphorus was also monitored in the process.

The ED removals showed to be dependent of EOCs characteristics and cell design. Removals were higher when using an AEM (60–72%) than a CEM (8–63%), except for caffeine when the effluent was placed in the cathode, that did not show any removal. When using an AEM with the effluent placed in the anode compartment, all the EOCs (including caffeine) were removed between 57–72%, mainly through electrodegradation phenomena.

Regarding phosphorus, a polarity switch may be done to a 2 C-cell with a AEM, depending on the effluent final use. This technology is still in its first steps and, in both cases, further optimization of ED parameters is needed. Still, this technological innovation and cross-cutting research envisages the promotion of economic, social and environmental benefits.

1. Introduction

The emerging organic contaminants (EOCs) have been detected worldwide in the aquatic environment, being recognized as an environmental issue [1,2].

One of the prominent entry routes of EOCs is through wastewater treatment plants (WWTP) as they are not efficiently removed during the treatment steps. Due to the wide range categories of EOCs, their removal is also dependent on their properties [3]. The discharge of effluent to aquatic environment does not have specific legislation for most of the contaminants (Directive 2008/105/EC), and the continuous input of EOCs into surface water may cause adverse impacts in the environment even at low concentrations [1,4]. In addition, due to water scarcity, effluent has been extensively reused for various purposes in many regions of the world including landscape and agriculture irrigation [5]. Effluent reuse in agriculture also contributes to nutrients recycling, as phosphorus, alleviating pressure on over-exploited resources (e.g. phosphate rock, included in the EU list of 27 Critical Raw Materials). In this context, developing cost-effective technologies for EOCs removal from effluent is thus of great interest to public and the environmental health.

Among the various technologies that have been developed over the last decades, the so-called electrochemical advanced oxidation processes (EAOPs) have been under increased interest, as a promising class of advanced oxidation processes (AOPs) [6]. Literature reports the use of AOPs [7] such as ozonation [8], photocatalysis [9], UV [10], UV/H_2O_2 [11] and fenton [12] as effective on EOCs degradation in wastewater. The use oxidizing agents such as hydroxyl radicals (·OH, redox potential of 2.80 V/SHE) can oxidize organic contaminants. Hydroxyl radicals initiate a series of oxidation reactions then leading to the ultimate mineralization products CO_2, H_2O and inorganic ions. Moreover, ·OH have a short life-time, estimated as only a few nanoseconds in water [13], and so they can be self-eliminated from the treatment system. The electrokinetic process (EK) is based on the application of a low level direct current and due to water electrolysis, ·OH are continuously being generated. Due to the formation of hydrogen cations at the anode and hydroxide anions at the cathode there will be a pH decrease and increase, respectively. The electrodialytic (ED) process

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accounts with the use of ion exchange membranes (anion exchange membrane, AEM and cation exchange membrane, CEM). The AEM only allows the passage of anions and the CEM the cations [14]. Few studies tested the applicability of the ED process in WWTP with contaminants removal (e.g. metals) from wastewater [15] and sewage sludge ash [16]. More recently, the removal of EOCs was carried out using EK and ED in soil [17,18] and in sewage sludge using ED [19,20]. It was reported that soil slurry and sewage sludge in the cathode compartment separated from anode by an AEM was effective in decreasing EOCs levels. Some studies also show that this same setup is useful to mobilize solubilized P from the cathode to the anode compartment [21].

Still, to the best of our knowledge, no works have been published regarding EOCs removal from effluent using ED process.

In this work, the ED process was applied to effluent testing the 2-compartments cell with different configurations. As the aim is to develop a cost-effective electro-technology to decrease EOCs concentrations from the effluent in WWTP, five compounds with different properties were selected after a literature survey. The chosen EOCs comprise a neural stimulant (caffeine, CAF), an industrial chemical (bisphenol A, BPA), two estrogenic steroid hormones (17β-oestradiol, E2; 17α-ethinyloestradiol, EE2) and a sunscreen compound (oxybenzone, MBPh). All EOCs have been detected in influent and effluent samples worldwide at relatively high concentrations (ng/L - ug/L) [22]. The properties of the studied contaminants can be found in Table 1. As the destination of the effluent might be for soil irrigation and having in mind the nutrient recycling, phosphorus was also monitored along the process.

2. Materials and methods

2.1. Chemicals and standards

Solvents were from Panreac (Barcelona, Spain), Merck (Darmstadt, Germany) and Sigma–Aldrich (Steinheim, Germany). Acetonitrile (ACN), methanol (MeOH) and acetone were HPLC gradient grade and formic and acetic acid were LC/MS grade. Deionized water further purified with a Milli-Q plus system from Millipore (Bedford, MA, USA) was also used. Sodium hydroxide (NaOH) were purchased from Sigma–Aldrich and sodium nitrate ($NaNO_3$) was from Panreac. Caffeine (≥90%), BPA (≥99%), E2 (≥97%), EE2 (≥98%) and MBPh (≥98%) were purchased from Sigma-Aldrich (Steinheim, Germany). Individual stock solutions for calibration purposes were prepared at 4000 mg/L in MeOH and stored at −18 °C.

2.2. Effluent sampling procedure

Effluent samples were collected at a WWTP from Simarsul located in Quinta do Conde, Sesimbra, Portugal. The WWTP has infrastructures with capacity to treat urban wastewater corresponding to about 94,000 equivalent inhabitants and the level of installed treatment is tertiary (UV light).

The WWTP has an aerobic reactor of suspended biomass to allow the biological treatment of wastewater. The effluent from this reactor goes to the secondary settling tank for phase separation where liquid samples were collected. Once at the laboratory, and to remove colloidal particles from the secondary effluent, the samples were pretreated using a 0.45-mm MF filter, and the filtered effluent was used in all experiments. Effluent samples were collected in May and June and initial characterization is presented in Table 2. Initial screening was done and none of the studied contaminants were detected in the collected samples.

Table 2
Characteristics of effluent samples.

Effluent sample Code (Eff#)	TSS mg/L	pH	Conductivity μS/cm	BOD_5 mg/L	COD mg/L	P mg/L
Eff1	17	7.31	947	6.1	47	11.5
Eff2	30	8.00	1880	30	150	5.8

2.3. Electrodialytic set-up

The 2-compartment (2 C) ED cell design was tested in accordance to designs presented in Fig. 1a–d. The 2 C ED laboratorial cell was assembled with two compartments (cathode and anode both with an internal diameter of 8 cm) separated by an ion exchange membrane [either an anion exchange membrane, AEM: AR204 SZRA B02249 or cation exchange membrane, CEM: CR67 HUY N12116B) both from Ionics Inc., Massachusetts, USA]. The electrodes were platinized titanium bars (diameter 3 mm) obtained from Permascand® and a power supply (Hewlett Packard E3612A) was used to maintain a constant current. The fresh electrolyte was a 10^{-2} M $NaNO_3$ solution with pH 6.4 (± 0.4) and conductivity of 1215 (± 62) μS/cm. The electrolyte was circulated by means of a peristaltic pump (Watson-Marlow503 U/R, Watson-Marlow Pumps Group, Falmouth, Cornwall, UK) in a closed circulation system.

2.4. Experimental set-up

Effluent was spiked with a mixture of 3 mg/L of each compound (CAF, BPA, E2, EE2 and MBPH) in 1:1 MeOH:Acetone. The effluent (300 mL) was placed in one of the electrode compartments. Electrolyte (500 mL) was put in the other electrode compartment and recirculated at 4 mL min^{-1}. Fig. 1a–d shows the different 2 C-cell configurations tested in the present work in which the (i) effluent was placed either in the anode or cathode compartment, and (ii) either a cation or anion exchange membrane were used for separating the compartments. The experiments were carried out for 12 h with current intensity applied of 20 mA. To assess EOCs removal kinetics, samples were collected hourly

Table 1
Chemical structure and properties of the emerging organic contaminants.

Compound	Caffeine	Bisphenol A	Estradiol	Ethinyl Estradiol	Oxybenzone
IUPAC Name	1,3,7-trimethylxanthine	4,4'-Isopropylidenediphenol	17β-estradiol	17α-ethinylestradiol	2-hydroxy-4-methoxybenzophenone
Category	CSN stimulant	Plasticizer	Estrogen	Estrogen	UV filter
Formula	$C_8H_{10}N_4O_2$	$C_{15}H_{16}O_2$	$C_{18}H_{24}O_2$	$C_{20}H_{24}O_2$	$C_{14}H_{12}O_3$
Molecular weight (g mol^{-1})	194.19	228.29	272.38	296.40	228.24
Solubility (mg L^{-1}) at 25 °C	2.16×10^4	120	3.9	11.3 (27 °C)	69
pKa[1]	14	9.6-10.2	10.7	10.3	7.6
Log K_{ow}[2]	−0.07	3.32	4.01	3.67	3.79
H (Pa m^3 mol^{-1})[3]	3.58×10^{-11}	1.0×10^{-6}	3.64×10^{-11}	7.94×10^{-12}	1.5×10^{-8}

References: http://pubchem.ncbi.nlm.nih.gov/, www.chemicalbook.com, http://SigmaAldrich.com.

[1] Ionization constant.

[2] Logarithm of the octanol-water partition coefficient.

[3] Henry's Law constant.

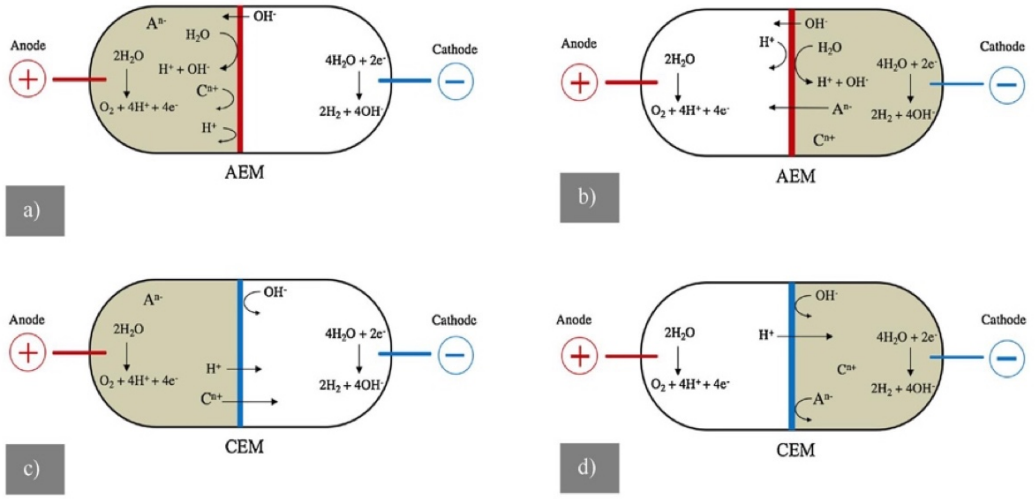

Fig. 1. Schematic representation of ED cell set-ups (a) A.AEM; (b) C.AEM; (c) A.CEM; (d) C.CEM.
Legend:
AEM: anion exchange membrane; CEM: cation exchange membrane.
Electrodialytic (ED) experiments:A.AEM and A.CEM: effluent placed in anode compartment using AEM and CEM, respectively. C.AEM and C.CEM: effluent placed in cathode compartment using AEM and CEM, respectively.

Table 3
Experimental design.

	Experiment CODE	Effluent sample Code (Eff#)	Effluent compartment	Membrane	Figure	Time (h)	I (mA)
Controls	Control.AEM	Eff1	*	AEM	–	12	0
	Control.CEM	Eff1	*	CEM	–		
ED experiments	A.AEM	Eff2	Anode	AEM	1a	12	20
	A.CEM	Eff2	Anode	CEM	1c		
	C.AEM	Eff2	Cathode	AEM	1b		
	C.CEM	Eff2	Cathode	CEM	1d		

Legend:
AEM: anion exchange membrane; CEM: cation exchange membrane;
A.AEM and A.CEM: effluent placed in anode compartment using anion and cation exchange membrane, respectively;
C.AEM and C.CEM: effluent placed in cathode compartment using anion and cation exchange membrane, respectively.

(total of 12 h). The control experiments without applied current were also carried out (one with anion, Control.AEM, and another with cation exchange membrane, Control.CEM, separating the compartments). The experimental design is shown in Table 3.

Conductivity, pH and the voltage drop between working electrodes were measured during the experiments.

For EOCs determination, initial and final samples were extracted following the procedures described in Section 2.5. For phosphorus analysis, electrolyte and effluent samples were collected at the beginning and at the end of each experiment and analyzed in accordance to Section 2.5 procedure.

All the experiments were carried out in dark conditions and at controlled room temperature (22 °C).

2.5. Samples analysis

For EOCs analysis in effluent and electrolyte, 200 mL of samples were pre-cleaned/concentrated by solid phase extraction, Oasis HLB; 200 mg, 6 mL (Waters; Saint-Quentin En Yvelines Cedex, France). The extracts were eluted with 2 × 3 mL of MeOH and, whenever needed, concentrated under a gentle stream of nitrogen. Determination was performed in Agilent 1260 Infinity II high-performance liquid chromatography (HPLC) equipped with a quaternary pump and auto-sampler (1260), and a diode array detector (DAD)/fluorescence detector 1100 Series. The RP-18e column (Chromolith High Resolution, 100 mm × 4.6 mm; VWR, Darmstadt, Germany) was used. All HPLC runs were performed at a constant flow (1 mL min^{-1}), in gradient mode, with the oven set to 38 °C. A mixture of ACN/Mili-Q water/Formic acid was used as eluents (A: 5/94.5/0.5% and B: 94.5/5/0.5%) with a gradient of 97% of A (0–15 min) followed by 95% of B, until 50 min, and 97% of A, until 55 min [20].

Calibration curve was performed in the range between 0.5 and 8.0 mg/L. The limits of detection and quantification in this work were, respectively, 0.55 and 1.7 μg L^{-1} for CAF, 0.7 and 2.1 μg L^{-1} for BPA, 1.4 and 4.2 μg L^{-1} for E2, 3.0 and 9.0 μg L^{-1} for EE2 and 0.8 and 2.4 μg L^{-1} for MBPh. Recovery tests were made with fortified effluent for 12 h of contact time. The recovery percentages were between 80 and 120% in all cases.

The HPLC was used to monitor the EOCs degradation rates and kinetics and to screen the formation of new peaks correspondent to new or related compounds. The identification of possible degradation products was carried out by GC/MS.

The P content was measured at 178.229 nm in an Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP–AES), Varian 720-ES. Mass balance in the different experiments varied between 80 and 120%.

3. Results and discussion

3.1. General results

The initial pH and conductivity of the electrolyte was 6.4 ± 0.3

Table 4
The pH, conductivity after ED treatment and voltage drop.

Experiment CODE	pH		Conductivity		Voltage drop	
	Effluent (Eff2)	Electrolyte	Effluent	Electrolyte	Initial	Final
A.AEM	1.49	11.80	3500	2100	7.8	5.7
A.CEM	1.81	10.95	1680	1555	8.4	7.7
C.AEM	9.79	1.70	1240	2300	9.8	8.9
C.CEM	11.80	1.54	1700	3200	7.9	5.9

Legend:
AEM: anion exchange membrane; CEM: cation exchange membrane;
A.AEM and A.CEM: effluent placed in anode compartment using anion and cation exchange membrane, respectively.
C.AEM and C.CEM: effluent placed in cathode compartment using anion and cation exchange membrane, respectively.

and 1352 ± 163 µS/cm, respectively. The pH and conductivity after the ED process and voltage drop are summarized in Table 4.

In the control experiments, there was no significant pH and conductivity change in the electrolyte and effluent. When the current was applied, water electrolysis at electrode compartments promoted a pH decrease in the anode compartment, due to the formation of H^+ ions, and a pH increase in the cathode compartment, due to the formation of OH^- ions. As so, when effluent was in the anode compartment the pH was acidic (range between 1.49 and 2.20) and when in the cathode compartment it was alkaline (between 9.79 and 12.10). However, depending on the used membrane, some exceptions were observed. In A.CEM the effluent pH only decreased to 4.5 as the used CEM allowed the migration of some H^+ ions from the anode (effluent) to the cathode. This migration also resulted in a pH decrease in the electrolyte [23].

The conductivity of effluent and electrolyte increased from the beginning to the end of the experiments.

The highest effluent conductivities were found when it was placed in the anode compartment using an AEM (A.AEM). This is explained by the formation of H^+ ions at the anode and migration of the OH^- and NO^{3-} from the cathode to the anode as they can pass through the AEM. Contrary, when a CEM was used with the effluent in the anode compartment (A.CEM) it only allowed the migration of cations out of anode, towards the cathode, thus the conductivity was lower at the end of the experiments comparing to the A.AEM (approx. less 55%). For C.CEM and C.AEM set-ups, the conductivity in the anolyte (electrolyte) was also higher than in the catholyte (effluent). The voltage drop behavior is in accordance with the changes observed in the conductivity. A slight variation of voltage between working electrodes was observed in all the cases, except in the control. According to Ohm's law, to a fixed current (20 mA in the present study), only a difference in the resistance could make the voltage change. If the voltage decreased, it means that the resistance decreased.

Other electrochemical reactions that occur in the anode and/or cathode compartments (oxidation and/or reduction) may also contribute to the conductivity and voltage changes. The EOCs can be degraded either in the effluent compartment or, if they migrate, in the electrolyte compartment. This degradation may cause the presence of more ions in solution, and consequently higher conductivity (as proved with the previous results of conductivity), thus decreasing the medium resistance.

3.2. EOCs removal in ED 2-compartment cells

The amount of contaminants not detected in effluent after ED in relation to the initial amount was considered as the amount removed. Calculations were performed according to Eq. (1).

$$\text{Removal}\,(\%) = \left(1 - \frac{PPCP\ concentration\ in\ the\ effluent\ after\ ED\ (mg\ L^{-1})}{PPCPs\ Initial\ concentration\ (mg\ L^{-1})}\right) \times 100 \quad (1)$$

After data analysis, only 1%, approximately, of the EOCs under study were detected in the electrolyte in all experiments, so, the removal percentage corresponds to approximately the degradation percentage.

The control experiments showed EOCs removals lower than 20%. Compound volatilization from effluent is not expected to be an important fate process based upon the estimated Henry's Law constant (H) of the compounds here studied ($H > 10^{-4}$) (Table 1). As the experiments were carried out in dark conditions, photodegradation is not a removal mechanism. Therefore, these removals were attributed to biotic factors as the effluent was collected after the secondary settling tank, which is the treatment after the biological reactor and prior UV disinfection step, and some microorganisms might still be present. Adsorption to the membranes may have also contributed to these values.

After the application of electric current (Fig. 2), CAF showed to be less susceptible to suffer electrodegradation not being removed when the effluent was placed in the cathode compartment (C.AEM and C.CEM). All the other studied compounds presented removal profiles more similar, although slight differences were observed. It was also expected that by putting the effluent in the anode compartment it would result in higher removals due to electrochemical anodic oxidation. The removal order was (excluding CAF): A.AEM ≈ C.AEM > A.CEM > C.CEM. This suggests that the type of membrane might influence the removals. In the A.AEM and C.AEM, the removal values

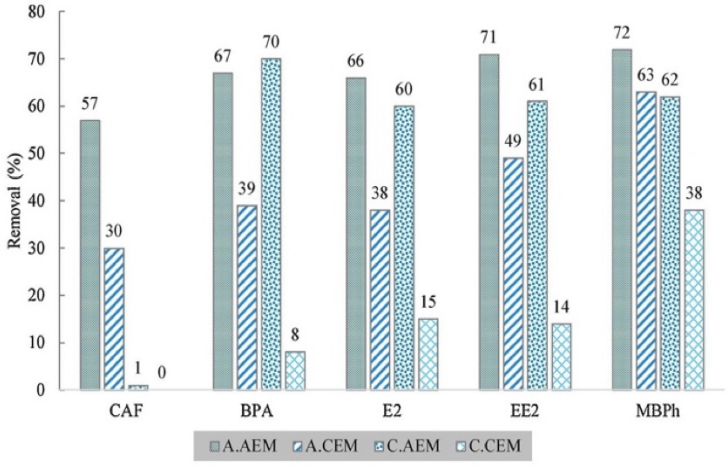

Fig. 2. EOCs removals (%) after ED process.
Legend:
AEM: anion exchange membrane; CEM: cation exchange membrane.
A.AEM and A.CEM: effluent placed in anode compartment using anion and cation exchange membrane, respectively.
C.AEM and C.CEM: effluent placed in cathode compartment using anion and cation exchange membrane, respectively.
CAF: caffeine, BPA: bisphenol A; E2: estradiol; EE2: ethinyl estradiol; MBPh: oxybenzone.

were, respectively, between 66–72% and 60–72% for BPA, E2, EE2 and MBPh, whereas in the A.CEM removals were between 30–63%. The lowest removals were achieved in the C.CEM, between 8–36% also for BPA, E2, EE2 and MBPh.

Two mechanisms are responsible for organics electrochemical degradation: (a) direct anodic oxidation, where the contaminants are adsorbed on the anode surface and destroyed by the anodic electron transfer reaction and (b) indirect oxidation in the liquid bulk which is mediated by the oxidants that are formed electrochemically; such oxidants include chlorine, hypochlorite, hydroxyl radicals, ozone and hydrogen peroxide [7]. Depending on the applied conditions, the oxidation promotes the contaminants mineralization to CO_2 and H_2O [24]. However, it should be mentioned that the by-products can be more harmful than the parent compounds and the establishment of the degradation pathways should be considered in future studies. The samples collected after the experiments were monitored by HPLC-DAD-UV and GC/MS and new peaks were not observed (not detected, < LOD).

The removals difference between the C.AEM (removals of 60–72%; CAF 1%) and C.CEM (removals of 8–38%; CAF 0%) may be explained by (i) pH changes in cathode and (ii) adsorption to the AEM. In the cathode, the pH of the effluent increased to values above compounds pKa, except for CAF (pKa = 14). This means that BPA, E2, EE2 and MBPh suffered deprotonation, being mainly present as anions, being thus able to electromigrate to the anode compartment through the AEM in the experiment C.AEM. Once in the anode compartment, compounds may suffer anodic oxidation through both the mechanism explained above. In this case, the presence of the CEM acts as a barrier as the anions cannot electromigrate to the anode compartment, after suffering deprotonation in the cathode.

It was found that organic foulants can contribute more to the fouling of the AEM than to the CEM. The greater fouling tendency of organics for the AEM may be explained by the electrostatic interactions between foulants and the membrane [25]. For example, proteins, which are amphoteric but normally negatively charged at a neutral pH, would be more attracted to the AEM. Also, polysaccharides containing hydroxyl groups could adsorb more onto the AEM than to the CEM [25]. Therefore, and although voltage increase due to fouling was not observed during the 12 h of ED experiments, a slightly yellow colour in AEM at the end of the experiments was observed, suggesting the adsorption of organic matter. In this sense, the presence of dissolved organic matter (humic substances) in the AEM may have promoted contaminants adsorption to the membrane, thus contributing to the high removals of contaminants with Log K_{ow} > 3 achieved in the C.AEM experiment. The CAF has a low Log K_{ow} (-0.07) and the highest solubility (2.16×10^4 mg/L) not being expected to adsorb into the AEM/organic matter.

The present data supports the importance of selecting the right membrane in ED for EOCs removal, as AEM presented a beneficial effect. Another factor influencing removals are the degradation mechanisms (pathways). In the anode compartment contaminants will suffer both direct and indirect degradation whereas in the cathode, only indirect degradation. Also, the pH in the anode compartment is acidic in which the hydroxyl radical has a standard reduction potential of 2.7 V whereas at alkaline pH it decreases to 1.8 V. Also, in a strongly alkaline solution, which is the case in the cathode, ·OH is rapidly converted to its conjugate base ·O-, pKa(·OH) = 11.9. When reacting with organic molecules ·OH behaves as an electrophile, whereas ·O- is a nucleophile. Thus. OH readily adds to unsaturated bonds but ·O- does not. If an aromatic molecule carries an aliphatic side chain, ·O- attacks there by H abstraction whilst. OH adds preferentially to the aromatic ring. The hydroxyl radicals and hydrogen atoms undergo similar types of reaction with organic molecules, but in abstraction from C−H bonds OH is more reactive and less selective than H (the formation of the H−OH bond is 57 kJ mol^{-1} more exothermic than the formation of the H−H bond) [26]. This might explain the lower EOCs removals (degradations) obtained in the cathode comparing to the anode (less 23–25%) specially CAF in which the tertiary amine seems to highly influence the results (0% removal in the C.CEM).

Once the ED process revealed positive results in the EOCs removal, as described earlier, it is believed that it could be set in a WWTP as a complementary treatment. Besides the technical feasibility, the economic feasibility needs to be also considered for any technology to be suitable for use in the industry. The costs associated with the effluent treatment by ED process are in the electricity and the membrane that might need to be changed/washed at some point. Considering an energy price of 0.15 €/kWh the energy costs (calculated through Eq. (2)) of treated effluent ranged between 1.1 and 1.8 €/m^3. Comparing to other treatments, also based on compounds oxidation, namely AOPs, the associated costs are in a range of 21.0 €/m^3 for UV/US/O_3 to 3 660.5 €/m^3 for US alone, 5.90 €/m^3 to 21.4 €/m^3 for US + UV treatment and US alone, respectively and 15.3 €/m^3 for US + UV + H_2O_2 to 3 346.4 €/m^3 for US alone. Also considering only the energy costs [27]. This shows that ED process is a competitive technology to be implemented in a WWTP as effluent polishing step avoiding the environment contamination and the risks for the human health through the discharge if EOCs contaminated effluent.

Energy consumption (KWh) = [Cell voltage (v) * Applied current (A)*Treatment time (h)]/1000 (2)

3.2.1. Removal kinetics for 12 h ED experiments

The Fig. 3a–d shows the normalized concentration as a function of time over the 12 h. Considering a pseudo first-order degradation for all the contaminants, the corresponding law rate can be written as follows: Ln(C/C0) = $-kt$, where k is the reaction apparent rate constant (Table 5). According with experimental data (Fig. 3a–d and Table 5), the EOCs removal follow a pseudo first-order kinetics (correlations, R^2, are higher than 0.9).

The highest removal rate constant was achieved in C.CEM for BPA ($9.22 \times 10^{-2}\,h^{-1}$) with a correlation of 0.9888 and the lowest was in C.CEM for E2 ($0.83 \times 10^{-2}\,h^{-1}$) with a low correlation (0.4061). EE2 in C.CEM also presents a lower correlation (0.7422). The obtained kinetics showed that the contaminants start to be removed immediately after the application of the electric current with pH changes in both cell compartments (20% decrease in the anode and increase in the cathode). Other authors also related the influence of pH in degradation kinetics e.g. the electrolysis carried out at different pH conditions pointed out that the degradation kinetics of both antibiotics were favored at acidic conditions [24]. The effect of initial pH solution in BPA degradation had a pronounced effect with the rate constant (k) increase with the initial solution pH drop from 7.3 to 5.5, 4.0 and 3.0 [3].

3.3. Phosphorus-recovery

Depending on the objective of treating the effluent, phosphorus should be found either in the cathode or the anode compartment at the end of the ED process application. Due to its economic value and utilization in agriculture as fertilizer, P should remain in the effluent for irrigation purposes. But, if the aim is to discharge the effluent, P concentration needs to be < 2 mg/L according to the Portuguese law, DL 348/98, November 9th; to achieve this target, P should be transported to the electrolyte compartment, from which it can be eventually separated, e.g. by precipitation, so that it can be further used.

Phosphoric acid molecule (H_3PO_4) can dissociate into three different species ($H_2P\,O_4^-$, $HP\,O_4^{2-}$ and $P\,O_4^{3-}$), which correspond to the acidity constants (pKa, at 298 K) 2.12, 7.2, and 12, respectively. So, if pH is kept under alkaline conditions (pH > 7), di- and trivalent species would prevail, implying a double or a triple amount of electrical current needed to move one phosphate ion when ED process is applied, and possibly higher energetic costs.

The percentage of phosphorus found in the anode or cathode end

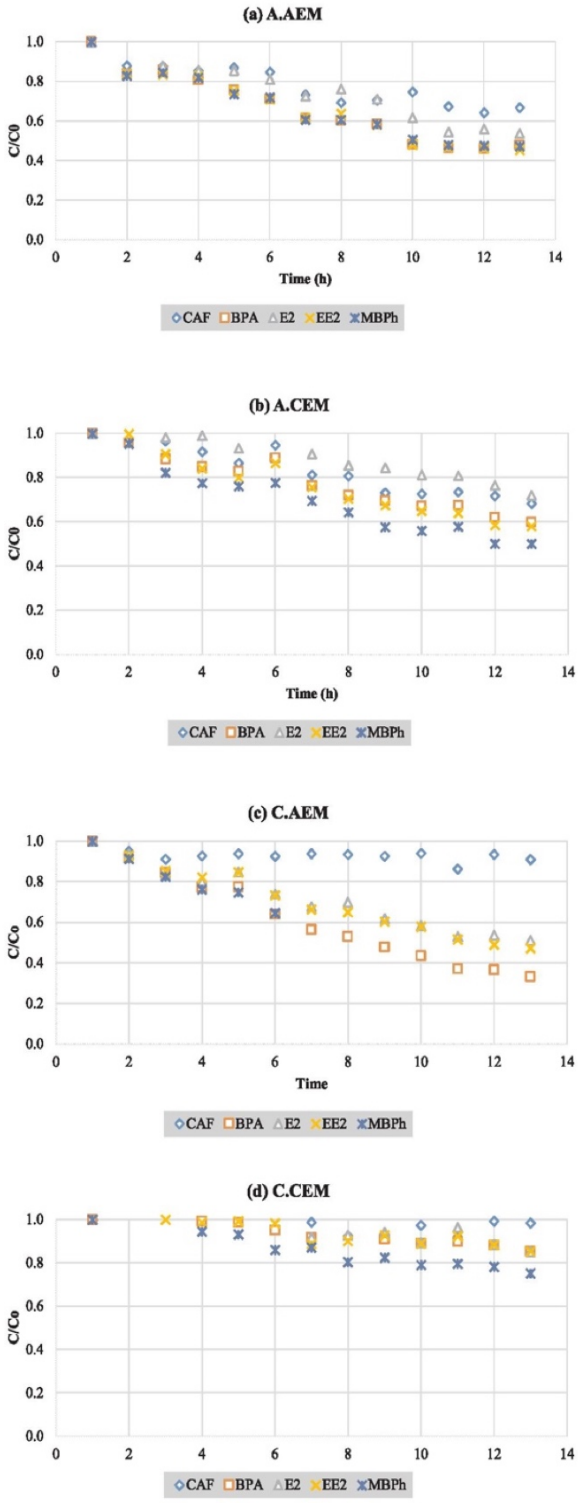

Fig. 3. Normalized EOCs concentration along the ED experiments: (a) A.AEM; (b) A.CEM; (c) C.AEM; (d) C.CEM.
Legend:
AEM: anion exchange membrane; CEM: cation exchange membrane.
Electrodialytic (ED) experiments:
A.AEM and A.CEM: effluent placed in anode compartment using AEM and CEM, respectively.
C.AEM and C.CEM: effluent placed in cathode compartment using AEM and CEM, respectively.
Emerging organic contaminants (EOCs):
CAF: caffeine
BPA: bisphenol A
E2: estradiol
EE2: ethinyl estradiol
MBPh: oxybenzone

Table 5
Pseudo first-order kinetics ($\ln(C0/C) = -kt$) of PPCPs removal through (k $x10^{-2}\ h^{-1}$).

Compound	A.AEM		A.CEM		C.AEM		C.CEM	
	k	R^2	k	R^2	k	R^2	k	R^2
CAF	3.96	0.8369	3.17	0.9205	*	*	*	*
BPA	7.12	0.9509	4.28	0.9545	9.22	0.9888	1.22	0.8233
E2	5.13	0.9147	2.27	0.8886	5.85	0.9674	0.83[a]	0.4062 [a]
EE2	7.15	0.9604	4.67	0.9665	6.32	0.9843	1.12 [a]	0.7422 [a]
MBPh	7.00	0.9541	6.12	0.9593	8.21	0.9926	2.40	0.9214

Legend: * no removal was observed; a: low correlation < 0.8.
AEM: anion exchange membrane; CEM: cation exchange membrane;
Electrodialytic experiments:
A.AEM and A.CEM: effluent placed in anode compartment using anion and cation exchange membrane, respectively;
C.AEM and C.CEM: effluent placed in cathode compartment using anion and cation exchange membrane, respectively.
Emerging organic contaminants:
CAF: caffeine, BPA: bisphenol A; E2: estradiol; EE2: ethinyl estradiol; MBPh: oxybenzone.

Table 6
Amount of phosphorus present in electrolyte after ED.

Experiment CODE	Electrolyte (%)
A.AEM	0.4
A.CEM	0.3
C.AEM	14.4
C.CEM	1.8

Legend:
AEM: anion exchange membrane; CEM: cation exchange membrane;
A.AEM and A.CEM: effluent placed in anode compartment using anion and cation exchange membrane, respectively;
C.AEM and C.CEM: effluent placed in cathode compartment using anion and cation exchange membrane, respectively.

was calculated based on the initial P present in the effluent (11.5 mg/L), and it can be seen in Table 6. In all experiments, P mostly remained in the effluent after 12 h of the ED process application. When the effluent is placed in the anode compartment, P remains in the effluent, because the acidic pH promotes neutral or monovalent phosphate forms (H_3PO_4/ $H_2P\ O_4^-$). In contrast, in the cathode compartment, the pH of the effluent becomes alkaline (> 8), where phosphates are mostly present in their divalent and trivalent anionic forms (HPO_4^{2-}/P O_4^{3-}), which facilitates their electromigration to the anode compartment. Using AEM (C.AEM), 14.4% of total P electromigrated to the anolyte, contrary of what happened when a CEM was used (C.CEM), as this membrane hinders the electromigration of negatively charged phosphates. Having in mind the reuse of effluent in agriculture, the best cell design seems to be A.AEM as high EOCs removal were also achieved. If the aim is to discharge the effluent to receiving waters, and therefore a low P content is required, the best option seems to be C.AEM. In this sense, an ED reactor with an anion exchange membrane with polarization control switch seems to be a promising technology for WWTP

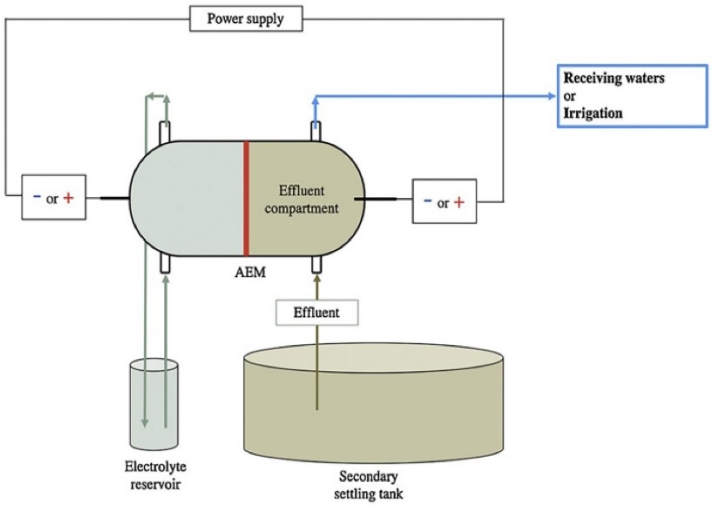

Fig. 4. Electrodialytic effluent treatment apparatus in which polarity is defined according to effluent desired final use.

application (Fig. 4). This system allows the WWTP operators to define the polarization of the effluent compartment according to effluent final desired use: (i) agricultural irrigation – anode, so that phosphorus remains in the effluent, thus producing a fertilizer solution; or (ii) discharge the effluent to receiving waters – cathode, so remaining P is recovered in the electrolyte (anode end, through electromigration). Moreover, an important advantage for the WWTP is the simultaneous EOCs removal and nutrient (in this case P) recovery. Still, in both cases, further optimization of ED parameters is needed to improve simultaneous EOCs degradation and P migration to the anolyte (electrolyte).

4. Conclusions

The results obtained in this work enable to conclude that the type of membrane (AEM vs. CEM) and the location where the effluent is placed had influence in the removal of EOCs.

Removals were higher when using an AEM (60–72%) instead of a CEM (8–63%) for all EOCs, with the exception of CAF when the effluent was placed in the cathode compartment, where there was no removal in any of the experiments. The best removals were achieved when effluent was placed in the anode compartment and an AEM was used, between 57 and 72%, mainly through electrodegradation phenomena.

Compounds characteristics also influenced the removals. CAF, which has a high solubility, low Log K_{ow} and high pKa (14), was the compound with the lowest removal in the anode compartment, not being removed in the cathode compartment, whereas MBPh (solubility = 60 mg/L and Log K_{ow} = 3.79) presented the highest removal in all experiments.

Regarding phosphorus, the present results showed that ED is a promising technology for its recycling, with the best results achieved when AEM were used. At the same time, the studied setup provides flexibility, as it allows to choose the polarity of the electrode in contact with the effluent, depending on the final use: (i) anode for agricultural irrigation, so that phosphorus remains in the effluent or (ii) cathode in case of discharge the effluent to receiving waters, so that remaining P is recovered in the electrolyte (anode). Thus, a removal of EOCs and P recovery are achieved simultaneously with ED process but still further optimization is needed.

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PAPER IV *Remediation of As – comparison of two different electrodialytic cells and applicability of treated soil in brick materials (conference paper)*

International RILEM Conference on Materials, Systems and Structures in Civil Engineering
Conference segment on electrochemistry in civil engineering
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Remediation of As - comparison of two different electrodialytic cells and applicability of treated soil in brick materials

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Abstract

An electrodialytic process (ED) was applied to clean-up an industrial soil from wood preservation polluted with arsenic (As). Two different cell-conditions were tested, in a 2-compartment cell set-up, using stirred soil suspensions. The experiments were carried out during 14 days, applying a constant current intensity of 5 mA. In addition, after ED a possible reuse of the soil for clay bricks was tested. The best result in the removal of As from suspended soil was obtained when suspended soil was placed in cathode compartment and the pH of the anode was maintained alkaline (pH ≈ 10). This setup showed efficiency to remove 74% of As towards the anolyte. In the other setup the soil suspension was kept in anode compartment and the pH of the catholyte was maintained acid (pH ≈ 2). This setup only achieved 3% of As removal towards the catholyte. These results showed that alkaline conditions favored the As desorption from soil to water and that the main transport mechanism was electromigration through the anion exchange membrane towards the anolyte. The treated soil proved to be an option to be used in bricks, which is also an advantage in the management process of soil residue.

Keywords: Arsenic, electrodialytic remediation, electromigration, soil pollution.

1. Introduction

Arsenic (As) is one of the elements of major environmental concern due to its highly toxicity to all forms of the life [1]. Arsenic is a natural element with features intermediate between metals and non-metals [2]. Arsenic contamination has been reported worldwide and is cited as the most hazardous substance by the USA Agency for Toxic Substance and Disease Registry [3] and is considered one of the priority pollutants by the US EPA and the EU. The sources of As can be natural (i.e. through dissolution of As compounds adsorbed onto pyrite ores into the water by geochemical factors) and anthropogenic (i.e. through use of insecticides, herbicides, phosphate fertilizers, mining and smelting, industrial processes and coal combustion) [2]. These sources of As can damage the health of the surrounding environments and increase the risk of soil, a serious environmental hazard. According to the U.S. Environmental Protection Agency the permissible limit of As in soil is 24 mg kg^{-1}.

Electrokinetic remediation (EKR) is a technique used to clean up waste matrices under the influence of an electric field generated between electrodes which induces different transport mechanisms (electroosmosis, electromigration and electrophoresis) and electrochemical reactions (electrolysis and electrodeposition) [4,5]. Electrodialytic remediation (EDR) adds the electrodialysis to the process, by the use of ion exchange membranes that act both as physical and chemical barriers. By the use of ion exchange membranes, the main direction for the electromigration within the polluted matrix is determined to be out of the soil. The EDR was developed at the Technical University of Denmark in 1992, was patented in 1995 (PCT/ DK95/00209), and has proven to be efficient in removing a wide range of contaminants, such as heavy metals [6], polycyclic aromatic hydrocarbons [7] and polychlorinated biphenyls [8] from suspended soils. The success of EDR is reported to be dependent on the specific site conditions, including the type and amount of contaminant, soil characteristics, organic content, as well as experimental conditions such as stirring and pH [5,9].

In the present study, the ED process was applied to a soil contaminated with As in a two-compartments cell design (2C). The feasibility of inserting the soil suspension in the anode or cathode compartment together with pH adjustment (alkaline in anolyte and acid in catholyte). The potential reuse of EDR treated soil in brick was also assessed.

2. Materials and methods

2.1 Experimental soil

The soil used in the present study was sampled from Collstrop site, located in an industrial area in Denmark. Collstrop soil is highly polluted with As provided by wood preservation activities.

2.2 Soil characteristics

The soil was analyzed for the following parameters: As concentration, pH, conductivity, carbonate and organic matter content. Laser and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) analysis was also carried out.

Arsenic concentration was determined according to the Danish Standard 259 [10]. Briefly, 1 g of dry soil was extracted with 20 mL HNO_3 and heated at 200 kPa (120 ºC) for 30 minutes. The liquid phase was separated from the solid particles by vacuum filtration (0.45 µm filter) and

diluted till 100 mL. Arsenic concentration was determined by inductively coupled plasma - atomic emission spectrometer (ICP-AES).

Soil pH was measured by suspending 5 g of dry soil in either 20 mL 1 M KCl or in distilled water and measured using a Radiometer pH electrode. Conductivity was measured using a CMD2010 conductivity meter after suspending 10 g of dry soil with 25 mL of distilled water followed by 30 min of agitation on a shaking table.

Carbonate content was determined volumetrically by the Scheibler method (2.5 g of soil reacting with 20 mL of 10% HCl). The amount was calculated and all the present carbonate was assumed as calcium carbonate. Organic matter was determined by loss on ignition after 1 h at 550 ºC.

SEM analysis was performed on the untreated and treated soil.

2.3 Desorption of heavy metals as a function of pH

The effect of pH in As desorption was assessed by suspending 2.5 g dry soil in 25 mL of HNO_3 or 25 mL NaOH with concentrations ranged between 0.01 M to 1.0 M followed by shaking during one week. The samples were made in duplicate. Extractions in distilled water were made as reference. After desorption tests, samples were filtered (0.45 μm), pH measured and As determined by ICP-AES.

2.4 Experimental setup

A two compartment cell set-up (2C) was tested varying the position of contaminated soil (Figure 1A and 1B). The cells were made from polymethyl methacrylate. The compartment where the suspended soil was placed had a L=10 cm and the electrolyte compartment a L=5 cm. Each cell had an internal diameter of 8 cm. Ion exchange membranes separating the central compartment from the electrode compartments were from Ionics, anion exchange membrane (AEM, AR204 SZRA B02249C) and cation exchange membrane (CEM, CR67 HUY N12116B). The electrodes were platinized titanium bars, with a 3 mm diameter (Bergsøe Anti Corrosion A/S, Herfoelge, Denmark). A power supply (Agilent E3612A) was used to maintain a constant current. The fresh electrolyte (500 mL of 10^{-2} M $NaNO_3$) was circulated in a closed system ("Pan World" magnetic pumps from Plastomec Magnet pump model P05). The electrolyte was conditioned at the beginning of the experiment, and whenever necessary, to achieve an acidic (pH=2) or alkaline pH (pH=10), depending on the applied treatment.

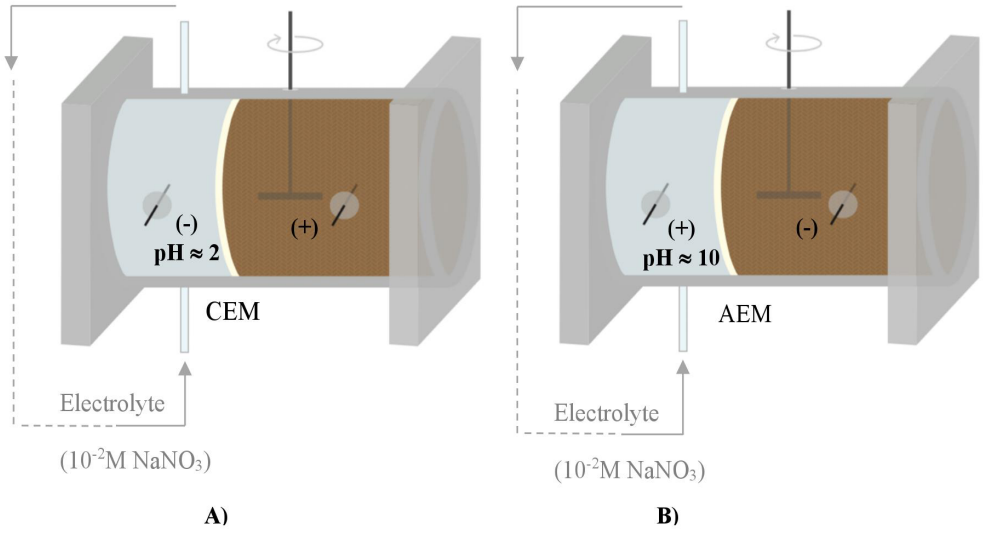

Figure 1 - Schematic presentation of the laboratory 2C cell used in experiments: A) soil suspension in the anode compartment, CEM, and catholyte pH adjusted to 2; B) soil suspension in the cathode compartment, AEM, and anolyte pH adjusted to 10.

2.5 Electrodialytic experimental conditions

Two electrodialytic experiments were performed (Table 1). One cell compartment was filled with 50 g of soil and 350 mL of distilled water corresponding a liquid/solid ratio of 7. In treatment 1 (T1) the suspended soil was kept in the anode compartment, a CEM was used to separate compartments, catholyte pH was adjusted to 2 throughout the treatment (Figure 1A). In treatment 2 (T2) the suspended soil was kept at the cathode compartment, an AEM was used to separate compartments, and anolyte pH was adjusted to 10 (Figure 1B).

The voltage between working electrodes, conductivity and pH of both cell compartments were measured twice a day. The pH of the electrolytes was adjusted whenever needed by addition of HNO_3 (1:1) and NaOH (6M).

At the end of the ED experiments, the suspended soil was drained using filter paper aiming to separate the solid from the liquid phase. The water content was measured. The soil solution was then filtered (0.45 µm) and the solid phase dried until constant weight (105 ºC), crushed by hand and extracted (analysis description in section 2.2). Membranes and electrolytes were soaked in 1 M and 5 M HNO_3, respectively, for 24 h to release metals and the liquid phase filtered (0.45 µm). The As concentration in the different parts of the cell (soil, soil solution, electrolyte, membrane, electrodes) was then determined by ICP-AES.

Table 1: Experimental conditions of the treatments.

Treatment (T#)	Cell Type (see Figure 1)	Soil compartment	Liquid/Solid (mL/g)	pH of electrolyte	Time (days)	Current (mA)
T1	A)	Anode	7	2	14	5
T2	B)	cathode		10		

2.6 Brick pellets

Pellets were made with EDR treated soil (T2) in order to study the suitability for further reuse in ceramics. Different amounts of soil were joined with pure clay (yellow wienerberger from soft-molded bricks) to test the stability of the pellets. The samples had a total weight of 2 g and 10 % of distilled water was added.

Brick pellets (2 cm in diameter) were made in a form and pressed to pellets in an Instron 6022 tester at 3.14 kN. The wet pellets were weighted before being heated at a furnace with a gradual temperature increase (until 1025 ºC) where they were kept by 1 h. After cooling to room temperature, the fired pellets were weighted and characterized by porosity, density and leaching (Section 2.6.1.).

2.6.1 Parameters of brick pellets

Aiming to determine porosity and density, the brick pellets were placed in a desiccator under vacuum for 3 h (100 N m^{-2}). After this time, the desiccator was filled with deionized water and pellets left for 1 h. The desiccator was then opened to the air during 1 day. The pellets were weighed over and under the water [11].

The leaching of As was also tested according to DS/EN 12457-3 [12]. The fired pellets were crushed and distilled water was added, liquid/solid ratio of 2. The suspension was agitated for 16 h and the liquid phase separated from the solid particles by vacuum filtration (0.45 µm). As concentration was determined by ICP-AES.

3. Results and discussion

3.1 Soil characteristics

The characteristics of the soil are listed in Table 2. The soil has a sandy loam texture. The initial concentration of As was 594 mg/kg. Like was expected according with literature [13], the pH of the soil in distilled water was of 6.3 whereas pH in KCl was of 5.4. The conductivity of the soil was of 0.2 mS/cm.

Table 2: Initial characteristics of Collstrop soil.

Type of soil	As (mg/kg)	pH_{KCl}	pH_{H2O}	Conductivity (mS/cm)	Carbonate content (%)	Organic matter (%)	Grain size distribution (%)		
							Clay	Silt	Sand
Sandy Loam	594 ± 100	5.4 ± 0.05	6.3 ± 0.3	0.2 ± 10	2.2 ± 0.04	19 ± 1	6	43	51

3.2 Desorption of As as a function of pH

The concentrations of As extracted from soil at different pH values is shown in Figure 3. In distilled water 61 mg/kg of As was extracted.

The results showed that As is desorbed from soil under highly acid ($0.1<pH<0.4$) and alkaline ($8<pH<13$) pH values. The lower pH values (0.1-0.4) released ≈514 mg/kg of As whereas the higher pH (≈13) released 533 mg/kg.

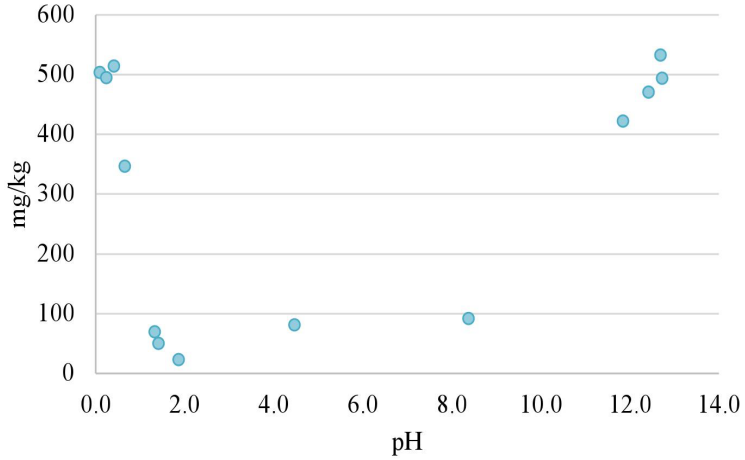

Figure 3 - Arsenic desorption as a function of pH.

3.3 SEM analysis

Figure 2 shows the differences in soil particles before and after EDR treatments. The largest changes in shape/morphology occurred in T2 where the suspended soil remained in cathode. This means that higher pH values may have influenced particles distribution. In T2, the small particles are adsorbed onto the surface of the largest ones forming aggregates (Figure 2 *iii*) whereas before EDR treatment (Figure 2 *i*) or in T1 (Figure 2.*ii*) the small particles are separated from the other particles.

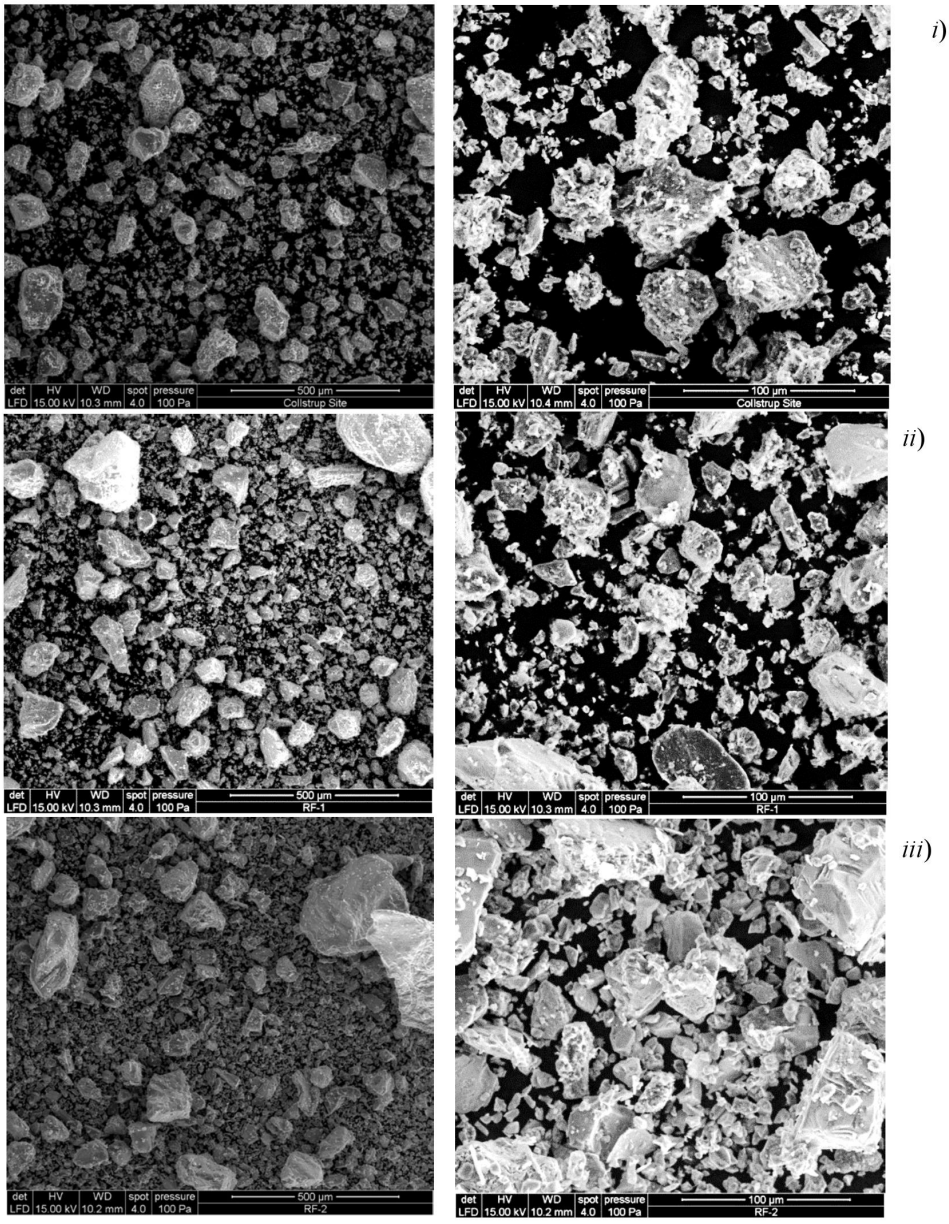

Figure 2 - SEM picture of Collstrup soil before EDR (*i*) and after EDR treatments under acid, T1 (*ii*) and alkaline, T2 (*iii*) conditions.

3.4 Electrodialytic experiments

3.4.1 General results

The voltage, conductivity and pH of the soil suspension during the EDR experiments are shown in Figures 3, 4 and 5, respectively.

Both treatments presented a similar behavior in voltage. From the beginning of the treatment until day 8, the voltage gradually dropped followed by a stabilization tendency. This pattern is probably because ions from electrolysis at the electrodes (H^+ or OH^-) decreased the conductivity in the suspension in the first phase.

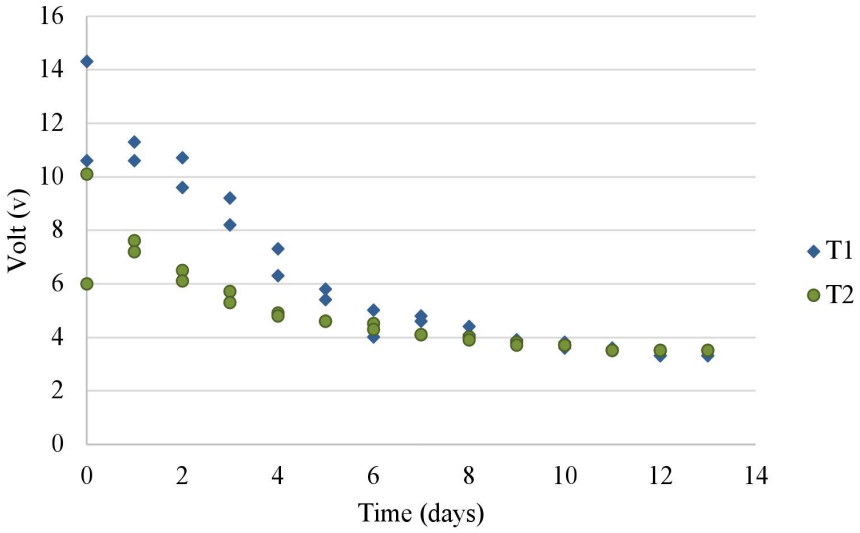

Figure 3 - Voltage over the cells during the EDR treatment

The electrical conductivity (Figure 4) increased in both treatments, corroborating voltage decrease due to a decreased electrical resistance (e.g. due to H^+ and OH^- produced from water electrolysis).

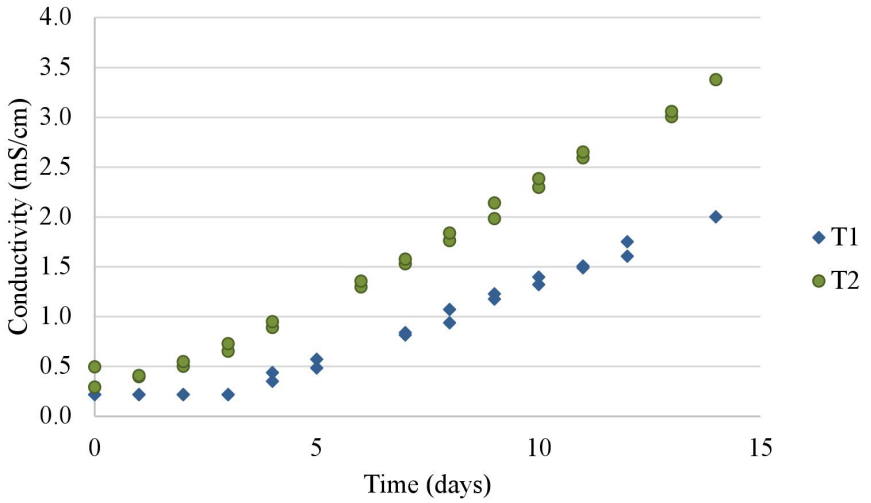

Figure 4 - Conductivity variation in the soil suspension during the EDR treatment.

The pH in the soil suspension is shown in Figure 5. When the soil suspension was placed in the anode (T1) the pH decreased until ≈2 whereas when placed in the cathode (T2) it increased to ≈11. The pH changes are due to water electrolysis, resulting in the formation of H^+ in the anode and OH^- in the cathode compartment.

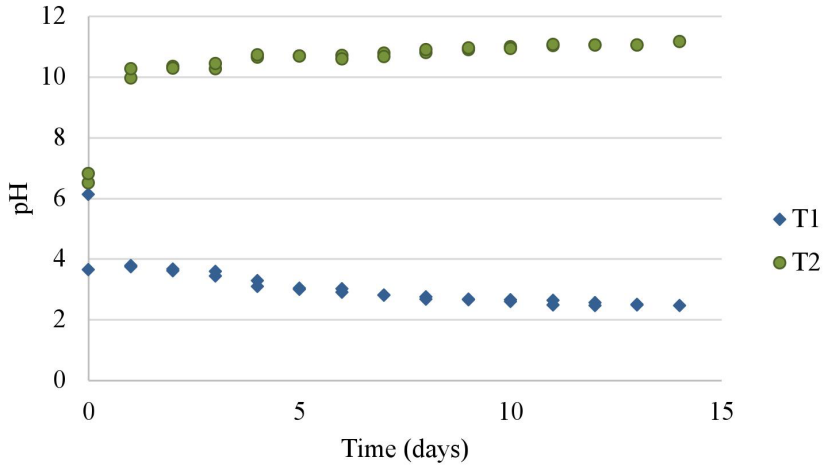

Figure 5 - pH variation in the soil suspension during EDR treatment.

3.4.2 Electrodialytic arsenic removal

An overview of As removal after EDR treatment is given in Table 3. The removed As is defined as the element found in the electrolyte compartment and in the ion exchange membrane. The removal percentage is calculated dividing the mass of element removed (electrolyte + membrane) by the final mass found in it (soil + soil solution + electrolyte + membrane). The

mass balance ranged between 77% and 99%. The As distribution in the different parts of cell after the ED process is shown in Figure 6. Also, the distribution pattern of As differed significantly when compared with acid and alkaline pH cell-conditions.

Table 3: Overall results of EDR of soil.

Treatments (T#)	**Removal efficiency** (%)	**Amount removed** (mg/kg)	**Mass balance** (%)
T1	3	31	99
T2	74	502	77

The EDR with acid cell-conditions (T1) resulted in 3% of As removal, corresponding to 31 mg/kg whereas the in the presence of alkaline cell-condition (T2) 74 % of As were removed towards the anode compartment corresponding to 502 mg/kg of As.

The soil suspension in the anode compartment (T1) was subject to oxidizing conditions and due to the CEM, only the movement of cations towards the catholyte was allowed which, in turn, was acidic due to pH adjustment (neutralization of OH^- by H^+ addition). At the final pH achieved in anode compartment of T1 (pH 2), As presented a weak soil desorption (see Figure 6) but also the typical negative charge at this pH ($H_3AsO_4+H_2O \Leftrightarrow H_2AsO_4^- + H_3O^+$, pka=2.20) limits its migration through CEM towards catholyte, as the prevailing As species is uncharged. Arsenic desorption is highly dependent on pH and redox potential conditions which influences its chemistry and composition [14]. Arsenic is a metalloid, which the primary forms in soils are arsenate-As(V) (H_2AsO_4) in oxidizing environment and arsenite-As(III) (H_3AsO_3) in reducing environments [15]. The experiments made so far were conducted in open laboratory cells with stirring and As(V) is expected to be the primary form and the main stable specie in an oxidizing environment. At neutral to acidic pH, the uncharged specie (H_3AsO_3) is expected to be present and therefore it will not be able to electromigrate [14]. From the 10% of As desorbed from soil to water (at pH 2), only 3% was able to pass through the CEM towards the catholyte. Ottosen et al. (2000) [14] reported that the efficiency of EDR treatment increased for As removal at low pH by adding an enhancement solution in order to desorb As from the soil.

The T2 treatment showed high (74%) As removal which is explained by the high As desorption at the pH achieved in the cathode compartment (pH 11). The presence of the AEM allowed the migration of As towards the anolyte, due to its negative charge under this chemical conditions. During the ED process, NaOH was added to the anolyte to keep the pH alkaline (≈10) at both sides of the membrane.

Despite the 74% of As removal in T2, the EDR treated soil still contained approximately 150 mg/kg of As. The application of this soil in construction material was tested aiming to optimize the re-use of industrial contaminated soil.

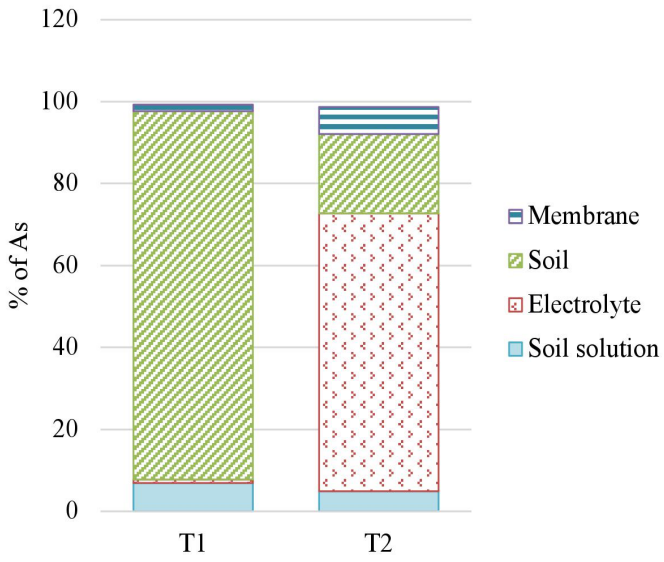

Figure 6 - Distribution of As after EDR treatments under acid, T1, and alkaline, T2, conditions.

3.5 Brick pellets

Figure 7 shows the brick pellets made with different amounts of soil. Due to the insufficient particle aggregation observed in pellets constituted by 100 % of treated soil, clay was joined at different amounts (50%, 75% and 90%). Clay minerals brought plasticity to the bricks showing consistence for all the tested percentages (50, 75 and 90%). Also, the brick pellets showed a different appearance (e.g. color) in accordance to the amount of clay.

The suitability of the brick pellets to be used as a constructed material was defined by porosity, density and As leachability (Section 3.4.1.; Table 4).

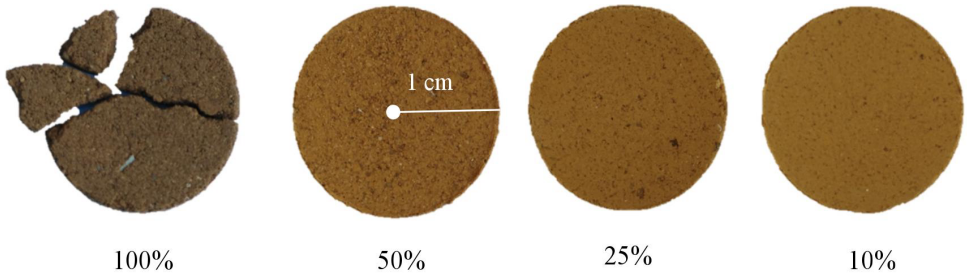

Figure 7 - Brick pellets with different amounts of soil (100 %, 50 %, 25 % and 10 %).

Porosity, which is directly related to the amount of water present, increased (between 27% to 34%) with the addition of clay to the brick pellets. This is explained by carbonates that decompose during sintering with gas releases conducting to pore formation in bricks [16].

Higher amount of pores means higher water absorption, which can reduce the brick resistance and durability. Regarding to dry matter density, the bricks showed to be very similar.

Leaching tests proved that As present in EDR treated soil was not released from the bricks. That means the use of treated soil as building material does not represent a risk to the environment, open a path to use this soil also for construction materials.

Table 4: Brick pellets parameters (mean ± SD).

Parameter	Amount of soil (%)		
	50	**25**	**10**
Porosity (%)	27 ± 1	32 ± 1	34 ± 1
Density (mg/m^3)	2.6 ± 0.1	2.7 ± 0	2.7 ± 0.1
Leaching (mg/kg)	ud	ud	ud

ud: under value

4. Conclusions

This work showed that the electrode compartment where the contaminated soil is located, is determining the As removal due to the prevailing pH changes. The set-up with suspended soil in the cathode compartment showed 74% of As removal towards the anolyte. The high pH of the cathode compartment promotes As desorption followed by electromigration through the AEM. The EDR treated soil may be further reused in ceramic bricks (together with clay) without risk of As leachability.

Acknowledgement

The present work was carried out in the labs at Department of Civil Engineering at the Technical University of Denmark. N. Couto also thanks Fundação para a Ciência e a Tecnologia for her Post-Doc fellowship (SFRH/BPD/81122/2011). The authors would like to thank Wan Chen for supplying the clay as well as the information about producing the brick pellets.

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PAPER V *Electrodialytic arsenic removal from bulk and pre-treated soil (Submitted)*

Electrodialytic arsenic removal from bulk and pre-treated soil

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Abstract

Arsenic (As) is a well-known highly toxic and carcinogenic element. A combination of electrodialytic remediation (EDR) and soil washing with flocculant addition for remediation of a soil polluted with As from wood preservation industry is the focus of this paper. The fine fraction from the washed soil after dry sieved was also considered.

The EDR experiments were carried out in a 2-compartments cell applying 0.01 mA/cm2 during 14, 7 and 3 days. The suspended soil slurry was placed in cathode compartment separated by anion exchange membrane (AEM) of the anolyte where the pH was kept at 10.

The soil was highly polluted with As and the EDR was able to remove between 50-80% corresponding to 400-478 mg As/kg of soil in 14 days. The higher amount of As was removed from the washed soil where the initial concentration was 784±10 mg As/kg of soil (1.3 times more than in original soil; $p<0.05$). However, in terms of removal efficiency, the pre-treated soil did not show a clear advantage prior EDR as the original soil showed 80% of As removal comparing with 61% and 50% for washed and fine fraction, respectively. Comparing 14, 7 and 3 days EDR, the major part of the As was removed within the first 3 days (63%) and ≈10% more of As was released doubling the time of the experiment: 71% in 7 days; 80% in 14 days.

Keywords: Arsenic; soil contamination; electrodialytic remediation; soil washing

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1. Introduction

Arsenic (As) is a metalloid naturally found in the environment, but its wide present in soils in problematic concentrations mainly due to human activities (Sauvé and Desrosiers 2014). It is leaked and accumulated to the soil during mining, smelting, agricultural use of pesticides and the disposal of industrial wastes (Chen et al. 2016). In addition, As pollution from wood preservation industry is a world-wide problem over the past several decades (Nico et al. 2004). High total and bioavailable concentrations of As in soils represent a potential risk for groundwater contamination and entry in the food chain (Arco-Lázaro et al. 2016). The adverse health effects and the negative environmental impact explains the recent increasing interest in As abundance, behaviour and remediation, and As is considered a legacy contaminant of emerging concern (Ungureanu et al. 2015).

Many researches have been conducted to develop physical, biological, thermal and chemical methods to allow the rehabilitation of contaminated sites (Guemiza et al. 2017), e.g. oxidation (Mondal et al. 2013), phytoremediation (Couto et al. 2015), soil washing (Cao et al. 2016) and electrokinetics (Kim et al. 2005). Among remediation technologies, soil washing including physical separation and chemical extraction is the most common technique used to extract heavy-metals or metalloids adsorbed onto soils (Jang et al. 2005). The washing water from the overall operation contain considerable concentrations of dissolved particles and consequently also As. Recirculation of the water during the soil washing is thus possible only after clean-up the washing solution where a flocculant can be added for a faster settling of the particles that float on top of the slurry (Kumpiene et al. 2017).

(Liao et al. 2016) showed that soil washing can be improved by a physical separation like sieving as it concentrates the metals in smaller volumes (the fine fraction) reducing the volume that needs to be handled. However, this fine fraction still need to be treated. (Sun et al. 2012) showed that treating the soil fines by electrodialytic process in 22 days, achieved higher As removal (64%) comparing with the original soil. However, the conditions need to be very specific as when doubling the current to 10 mA or changing the liquid solid ratio to 7 could the removal efficiency decreased. The electrodialytic remediation (EDR), has been investigated as a technique to clean up contaminated matrices under the influence of an electric field generated between electrodes and using ion exchange membranes to separate (physical and chemical) the contaminated matrix from the electrolytes (Couto et al., 2015; Guedes et al., 2016; Ottosen et al., 2003; Parés Viader et al., 2017). EDR soil remediation have been shown effective for metals removal from soils, but the remediation results show to be dependent of specific conditions, e.g. type of contaminants and pH. The EDR success in an un-enhanced three compartment system was reported limited, e.g. 35% of As removal was obtained from a Danish soil (Ottosen et al. 2009) and 51% As was removed from a Portuguese soil as best results (Ribeiro et al. 1998). By mixing ammonia into the soil, the removal improved and As was reduced from 900 mg/kg to 90 mg/kg in some parts of the Danish soil (Ottosen et al. 2009). Ammonia causes the soil to be alkaline and As is mainly present as negatively charged species in the alkaline environment and thus

As is mobile in the electric field. The obtained concentration however did not meet the limiting value in soils in Denmark (20 mg/kg) (Miljøstyrelsen (Danish EPA) 2015) where the polluted soil originated from, nor the even lower limiting value for the soil quality guidelines (12 mg kg-1) from Canadian Council of Ministers of Environment (CCME, 1997). Simultaneous removal of Cu, Cr, and As by EDR from soil suspended in ammonium citrate was in focus in (Ottosen et al. 2009), but even though the simultaneous removal was obtained to some extent (95% Cu, 74% Cr, and 61% As), the limiting value for As was not met. Previous published research underlines that As is among the pollutants, which is more difficult to remove from soil and different strategies have been study to enhance the removal rates. Another work on simultaneous removal of Cr and As by electrokinetics used sodium hypochlorite as assisting agent, which together with the hydroxide ions produced at the cathode created an oxidizing environment at high pH, oxidized Cr(III) to the more mobile Cr(IV), which forms anionic species in the alkaline medium where also As(V) is mobile (Hécho et al. 1998). The results showed that the use of an assisting agent forming alkaline environments accelerates As electromigration in/from the soil. In addition to an alkaline pH it is important to control pH of electrolytes in electrokinetic remediation. In (Ryu et al. 2011) and (Baek et al. 2009) it was shown in 3-compartment cell that anolyte condition using an alkaline solution enhanced the transport of As by electrokinetic remediation compared to an experiment without NaOH addition in the anolyte.

The purpose of the present work was to test the hypothesis of the advantage of soil washing and size separation prior to EDR. The work follows an initial study, where 74% (500 mg/kg) of As was removed from a soil polluted with As from wood preservation industry (Ferreira et al. 2016). The setup is designed so an alkaline pH is maintained in the treated soil suspension all through the treatment, as high pH has shown to achieve the best As removals in the experiments previously reported.

1. Materials and methods

1.1. Experimental soil

Soil was sampled from the top layer at an abandoned wood preservation site (the Collstrup site in Hillerød, Denmark).

The original soil was washed with water at a German industrial soil washing facility. The washing process consists of a series of mechanical separation steps in a closed system, where the soil slurry runs through, aiming to separate the coarse fractions from the fine fractions. The water is then recycled due to the addition of a flocculant in the 80 m3 of water in the closed system. The anionic polyacrylamide flocculant physically forms inter-particle bridges that draw colloids into larger aggregates, which leads to a faster settling of the fine particles and the possibility to separate them from the water. The flocculant is a high molecular weight anionic polyacrylamide flocculant supplied as a liquid dispersion grade (0.2% polymer-based flocculant, Magnafloc 120L from BASF).

The washed soil was dry-sieved in the laboratory and subjected to automatic shaking in a 0.063 mm sieve positioned in a vibrating screen instrument where the fine fraction was obtained.

1.1. Analysis of soil characteristics

The soils were characterized by the following parameters: As concentration, pH, conductivity, organic matter, carbonates contents and grain size distribution. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) analysis was also carried out.

The As concentration was measured after digestion following the method describes in Danish Standard (DS) 259 (Danish Standard DS 259 2003): 20.0 mL of 10M HNO3 was added in 1.00 g of dry soil and heated at 200 kPa (120 ºC) for 30 minutes. The liquid was separated from the solid particles by vacuum through a 0.45 µm filter and diluted to 100 mL. The As concentration in the filtrate sample was analysed by ICP-OES (inductively coupled plasma-optical emission spectrometry). A blank was analysed between samples to guarantee the quality of the results. In addition, quality control standard solutions were run periodically between the samples.

Soil pH was measured by suspending 5.00 g of dry soil in either 20 mL 1.0 M KCl or in distilled water. After 1 hour of agitation, pH was measured using a radiometer pH electrode. Conductivity was measured by suspending 10.00 g of dry soil in 25 mL distilled water and after 30 min agitation.

The content of organic matter was found as a loss on ignition after 1 h at 550 ºC. Carbonate content was determined volumetrically by the Scheibler method in which 2.50 g of soil reacts with 20 mL of 10% HCl. The carbonate amount calculated was assumed to be exclusively calcium carbonate.

The grain size distribution was obtained by means of laser diffraction method performed with Mastersizer 2000 (Malvern Instruments). The measurements were conducted in a liquid dispersion with a peptising agent.

1.2. Desorption of As as a function of pH

The effect of pH on As desorption was assessed by suspending 2.5 g dry original soil in 25 mL HNO3 or 25 mL NaOH with concentrations ranging between 0.01 M and 1.0 M. After filtration (0.45 µm), the As concentrations were measured in the liquid phase by ICP-OES. Extractions in distilled water were made as reference. Extractions were made in duplicate.

1.3. Sequential extraction of As

Sequential extraction was performed based on the improvement of the three-step method (also known as BCR), with an extra residual step. The method is described in Standards, Measurements and Testing Program of the European Union (Pueyo M Mateu J Rigol A Vidal M López-Sánchez J Rauret G 2008). The dried soil was crushed and 0.5 g was treated in four steps as follows: (1) exchangeable and acid soluble: extraction with 20.0 mL of 0.11 M acetic acid (CH3COOH) (pH 3) for 16 h, (2) reducible:

extraction with 20.0 mL of 0.1 M of hydroxyammonium chloride (NH2OH·HCl) (pH 2) for 16 h, (3) oxidizable: consists of a change from reducing to oxidizing condition and is performed by extraction with 5.0 mL of 8.8 M of hydrogen peroxide (H2O2) for 1h and heating to 85 ºC for 1 h with a lid followed by evaporation of the liquid at 85 ºC until it had been reduced to less than 1 mL by removal of the lid. The addition of 5.0 mL of 8.8 M H2O2 was repeated, followed by resumed heating to 85 ºC for 1h and removal of the lid for evaporation until almost dry. After cooling, 25.0 mL of 1 M (NH4)OOCCH3 (pH 2) was added, and extraction lasted for 16h, and (4) residual fractions: digestion according to DS 259 (described above). Between each step (excluding the residual fraction) the sample was centrifuged at 3000 rpm for 15 min, and the supernatant was decanted and stored for Varian 720-ES ICP-OES analysis. Before the addition of each new reagent, the sample was washed for 15 min with 10.0 mL of distilled water and centrifuged at 3000 rpm for 15 min, and the supernatant was then decanted and discharged. All extractions were performed at room temperature, and samples in each step were made in duplicate.

1.4. Experimental setup

The EDR experiments were carried out in a cylindrical Plexiglas-cells with two compartments (anode and cathode) with an internal diameter of 8 cm. The cathode compartment with the soil slurry was 10 cm, whereas the anode compartment was 5 cm long. The experimental cell is seen in Figure 1. An overhead stirrer was used to stir the soil slurry. The anolyte was circulated by a Plastomec pump model P05 between the chamber and a glass bottle. The anion exchange membrane from Ionics (AEM, AR204 SZRA B02249C) separated the compartments. The electrodes were platinized titanium bars (length of 5 cm and diameter of 3 mm) obtained from Permascand®. The power supply (Agilent E3612A) was used to maintain a constant DC current.

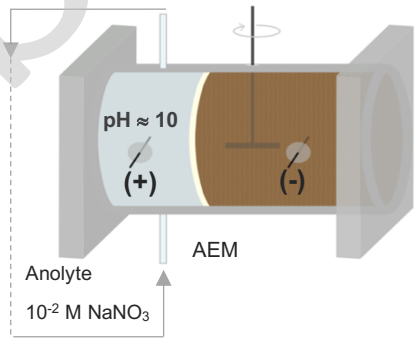

Figure 1 - Schematic representation of the electrodialytic laboratory 2-compartment cell used in experiments: anode compartment with pH adjusted to 10 and soil slurry in cathode compartment. The separation between soil slurry and anode compartment was made through an anion exchange membrane (AEM).

1.5. Electrodialytic experimental conditions

The EDR experiments were performed according to the conditions summarized in Table 1. The cathode compartment was filled with 50 g of dry soil and 350 mL distilled water corresponding to a liquid/solid ratio (L/S) of 7. The anolyte was 500 mL of 10-2 M NaNO3 with pH adjusted to 10. The pH was adjusted whenever needed with 5M NaOH solution. During the experiments, conductivity and pH in the soil slurry, and the voltage applied to the electrodes were measured twice every 24 h. The soil is termed "original" if it is not washed, and "floc" when it is the soil fraction received after washing at the German soil washing plant. The fine fraction obtained after dry-sieved the washed soil "floc" was named as "FF floc".

Table 1 - Experimental conditions

Experiment	Soil code	Pre-treatment	Time (days)	Current intensity (mA/cm^2)	L/S
1	Original	No	14	0.01	7
2	Floc	Washing	14	0.01	7
3	FF floc	Washing and sieving	14	0.01	7
4	Original	No	7	0.01	7
5	Original	No	3	0.01	7

At the end of the EDR experiments, the content of As in the different parts of the cell (membrane, electrodes, soil, water and anolyte) were analysed by Varian 720-ES Ion Chromatography Plasma (ICP-OES). The suspended soil from the central compartment was drained through filter paper to separate the solids from the liquid phase, and water content was measured too. The solid phase was dried (105 ºC), crushed by hand, digested and analysed as described in section 2.5. Membrane and electrodes were soaked in 1M and 5M HNO3, respectively, for 24h prior to analysing As in the liquid phase by ICP-OES.

2. Results and discussion

2.1. Experimental soil

The soil characteristics are listed in Table 2. The soil has a sandy loam texture (6% clay, 43% silt and 51% sand) with a low carbonate content, which means a low buffer capacity. The organic matter content was more than 10% and the pH is close to neutral being similar between all the studied soils. The pH values of soil suspended in KCl were lower (0.4-0.9 pH units of difference) comparing the pH measured in distilled water (H2O), as expected.

The analysis of the soil fractions showed that grain size distribution did not change as intended after washed in the industrial facility (Table 2). Visually it was evident, that the soil washing at the industrial facility had not been effective in separating the soil into a coarse fraction and a fine fraction, as sand was easily seen whereas the fine fraction was lumped together. Figure 2 shows the soil particles for the original soil and the washed soil analysed by SEM-EDX. Only after dry sieved in the laboratory, the fine fraction (content of silt and clay fraction, <0.063 mm) was obtained. The flocculant addition to faster settling the particles in suspension could have formed flocs with strong bridging mechanism making the size separation fraction through washing not so efficient. Attachment of small particles might be the reason of the inefficient size fraction separation in soil washing.

The site where the soil was collected was heavily contaminated with As. The As concentration in the original soil exceed the soil quality criteria in Denmark (20 mg/kg) by 30 times (Miljøstyrelsen (Danish EPA) 2015). The As concertation in original soil was significantly different ($p<0.05$) comparing with washed and fine fraction. However, between washed and fine fraction no differences ($p>0.05$) were found. In general, it can be expected that metal pollutants are concentrated in the soil fines due to the larger surface area and the higher number of adsorption sites, which is also the general basis for separating the soil into a non-polluted coarse fraction and a polluted fine fraction in soil washing methods. The similar concentration in washed and fine fraction can be explained by the fact that, the industrial soil in the present study had a very high concentration of As and surface adsorption processes might be overpowered by surface (co)-precipitation, which can occur on the particles of any size (Kumpiene et al. 2017). Other studies also showed the inefficiency of soil sieving systems in laboratory set ups, e.g. (Xu et al. 2014) and to have the higher pollutants concentrations in both 0.063 mm and fractions larger than 1.0 mm e.g., (Liao et al. 2016; Ottosen et al. 2009).

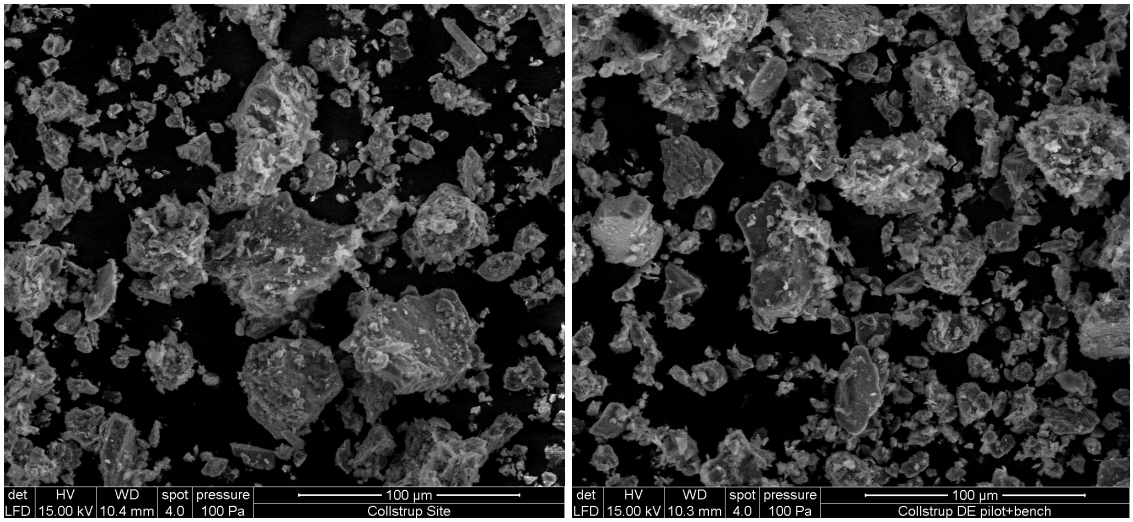

Figure 2 - SEM-EDX picture of a) original and b) washed soil.

Table 2 - Initial characteristics of soils in study

Soil code	Grain size distribution (%)			As (mg/kg)	pHKCl	pHH2O	Carbonate content (%)	Organic matter (%)
	Clay	Silt	Sand					
Original	6	43	51	594 ± 79	5.4 ± 0.05	6.3 ± 0.3	2.2 ± 0.2	19 ± 1
Floc	3	41	56	784 ± 5	6.3 ± 0.03	6.7 ± 0.3	1.5 ± 0.2	15 ± 3
FF floc	< 0.063 mm			804 ± 4	6.0 ± 0.3	6.2 ± 0.3		

2.2. Desorption of As as a function of pH

Figure 3 shows the concentrations of As extracted from the original soil and washed soil (coarse "floc" and fine fraction "FF floc") at different pH values. The results show that As is mainly (>80%) desorbed from soil under highly acid 0.1<pH<0.4 and alkaline pH values pH>12. In the alkaline region for pH>12, a higher As desorption was verified for the fine fraction "FF floc" when compared with low pH values.

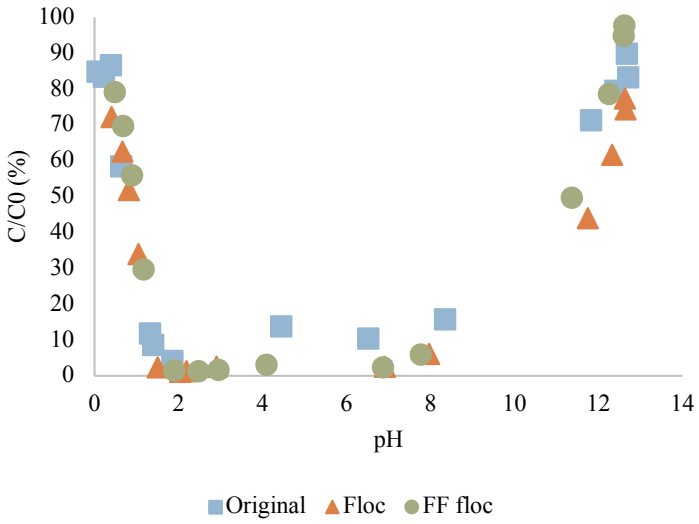

Figure 3 - Desorption dependency on pH of As in original soil, washed ("Floc") and the fine fraction from washed soil ("FF floc").

2.3. Electrodialytic experiments

2.3.1. General results

The pH of the soil slurry increased to 10 after 24h of applied current and faster increased to 11, remaining constant until the end of the EDR. The pH increase was due to the production of OH- ions at the cathode. The anion exchange membrane is not 100% ideal and thus some of the acid generate at the anode might pass to the soil slurry (Ottosen et al. 2000). With the pH adjustments, the pH increases fast as exchange of H+ ions from the anolyte and with other cations from the soil suspension is covered by NaOH addition (Ferreira et al. 2016). The voltage and conductivity of the soil slurry during the EDR experiments are shown in Figure 4 and 5, respectively.

The conductivity increased until the end for all the experiments due to the addition of OH-. The voltage behaviour was as expected from the conductivity results. "FF floc" experiments had higher voltage comparing with the other experiments because less ions were released and the electrical resistance across the cell increased. The feasibility of the conditioning anolyte with strong basic solution was study by (D. Kim et al. 2009) and (Baek et al. 2009) and less energy expenditure was registered comparing without pH adjustments. This fact shows to be an advantage for EDR as energy consumption use to be a critical factor to evaluate the feasibility of EDR.

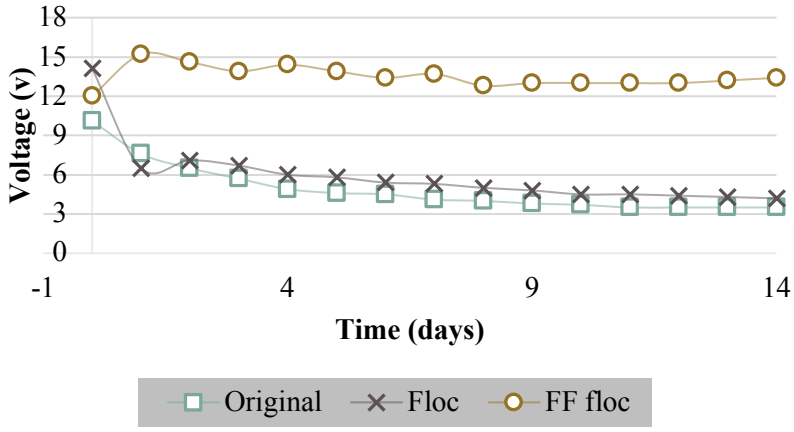

Figure 4 - Voltage over the cells during the EDR.

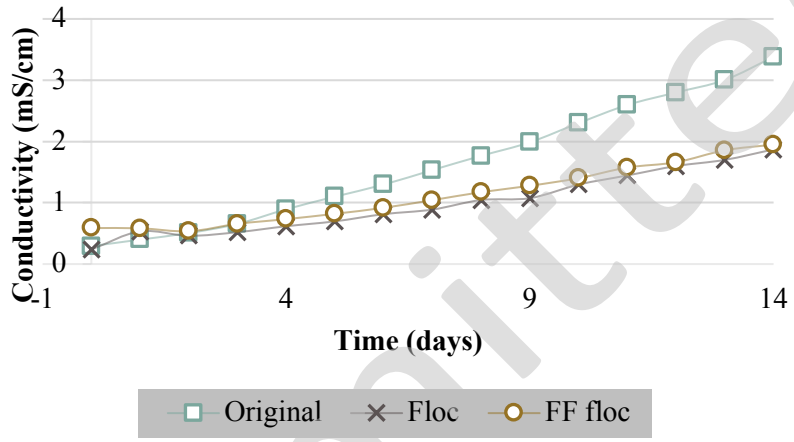

Figure 5 - Conductivity variation in the soil slurry during the EDR.

2.3.2. Electrodialytic As removal

An overview of the results obtained in the EDR experiments is given in Table 3.

The mass balance of As is defined as the relation between the sum of mass found in the different parts of the cell at the end of the experiment and the initial mass calculated on basis of the mean initial concentration (given in Table 2). The As removal in percentage is calculated as mass of all As at the end of the experiment minus the part in the soil divided by the total mass found in all parts of the cell at the end of the experiment. The mass balances ranged between 77% and 96%. This is considered an acceptable range because imperfect mass balances are expected considering inhomogeneous distribution of the As in the industrially polluted soil (Jensen et al. 2007).

Regarding to As removal, the results showed between 50% and 80% corresponding a 400 to 478 mg As/kg of soil by EDR. The oxygen and carbon dioxide concentrations in suspended ED cell can be assumed to be in equilibrium with the atmosphere, which allows for oxidation of As (III) to As (V) as

an oxyanion such as $H2AsO_4^-$, $HAsO_4^{2-}$or AsO_4^{3-}, which could be transferred to the anolyte. At pH between 7-11 in the soil slurry $HAsO_4^{2-}$ is expected to prevail (Wang and Mulligan, 2006). This anion will migrate to anolyte through the AEM under the applied electric field. The ligand displacement reaction of hydroxyl ions with As species and high pH conditions prevent the re-adsorption of the metalloid (Jang et al. 2005).

Comparing the removals between the three soils, the amount of As removed from original soil was higher (>20%) and mostly recovered in the electrolyte (Figure 6). Even though the concentration of As showed to be statistically ($p<0.05$) higher in washed and fine fraction, higher removals percentages were not achieved. The binding strength between soil particles and As before and after EDR was analysed by sequential extraction (Figure 7). The results show that As was mainly associated with the exchangeable and reducible phases before remediation for the three types of soil. The relative mobility of As obtained from the different soils was found in increasing order as: exchangeable< reducible<oxidizable<residual fraction. After EDR, most part of the As in the exchangeable fraction was removed during EDR, with the less available fractions (oxidizable and residual) increasing mainly for the pre-treated soils. This proves that removing As from original soil it might be easier because As is preferentially bound to Fe and Mn oxides (reducible fraction), instead of oxidizable (large fractions of sulphides) and residual fractions, which is reported to be more difficult to remove (Kim et al. 2001). Laboratorial studies are required in order to study the effects of flocculant addition in soil washing. The optimization of the washing soil step can increase the EDR efficiency as in theory, after washing less soil needs to be treated and consequently less remediation costs.

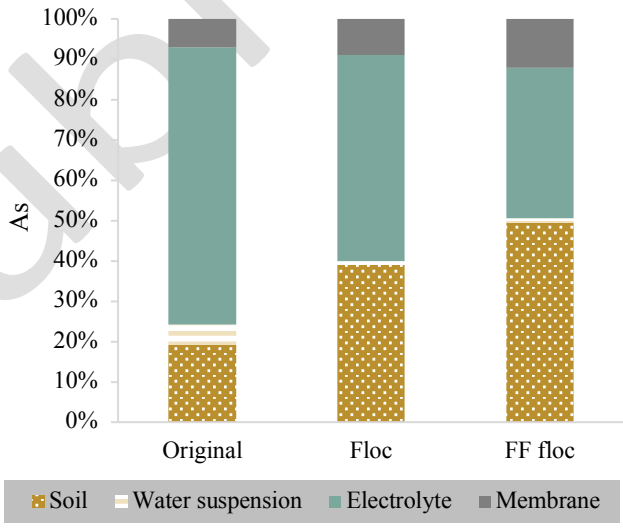

Figure 6 - Distribution of As in the different parts of the electrodialytic cell at the end of the EDR experiments.

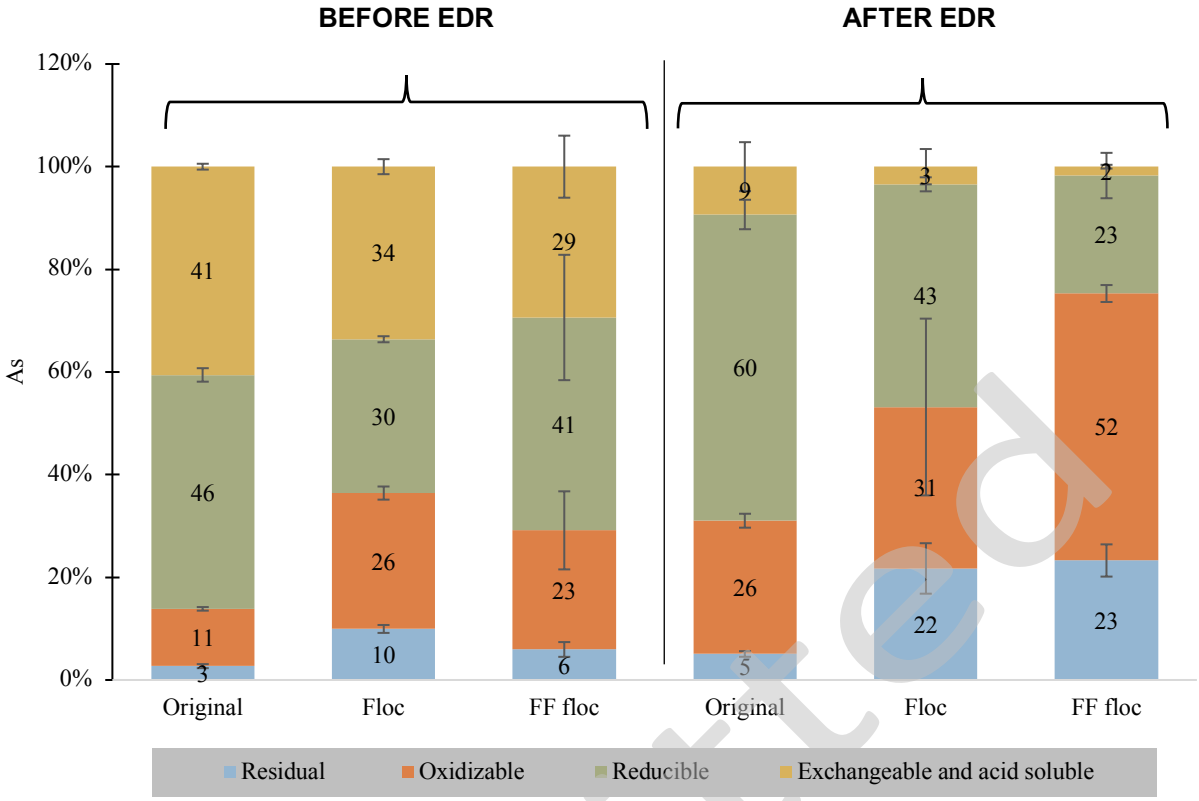

Figure 7 – As distribution in the different soil fractions in original soil, washed and fine fraction before and after EDR experiments analyzed by sequential extraction method (n=2).

2.3.3. Time influence in EDR of As

In order to make the EDR more efficient, different periods of time were tested. In the following experiments the original soil was chosen as the experimental sample. The mass balance of the experiments that last 7 and 3 days were 100% and 83%, respectively.

The final pH, conductivity and voltage range of the soil after EDR experiments can be seen in Table 4. The pH of the soil slurry was increased until 11 after 12h due the OH- generation in cathode compartment. The conductivity and voltage behaviour of the experiments were as expected. The voltage decreased during the experiments due the decreased in electrical resistance across the cell with the consequently increased of conductivity.

Table 4 - Final pH, conductivity and voltage drop for the experiments with 7 and 3 days

Experiment #	Soil code	Time	pHf	Condf (mS/cm)	Volti (v)	Voltf (v)
1	Original	14	11.2	3.4	10.1	3.5
4	Original	7	11.1	1.2	10.8	6.6
5	Original	3	10.9	0.5	13.0	7.9

An overview of the As removals for the experiments is given by Figure 8. Around 10% more of As was released doubling the time of the experiment: 80% in 14 days; 72% in 7 days and 63% in 3 days. The results show that most part of the As is released from soil within 3 days and is slowly desorbed from soil over the time. Appear the only 10% of difference between 7 and 3 days in As removal, 30% more of As was found in electrolyte and less 19% in membrane for the longest period. The presence of As in the membrane is not different when comparing the 14 and 7 days experiment (only 3% of difference) but 3 days did not show to be enough to migrate through the AEM towards anolyte. These results are promising because the same amount of As can be removed in short periods of time making the EDR more efficient, however further studies are needed to recover more As in the anolyte.

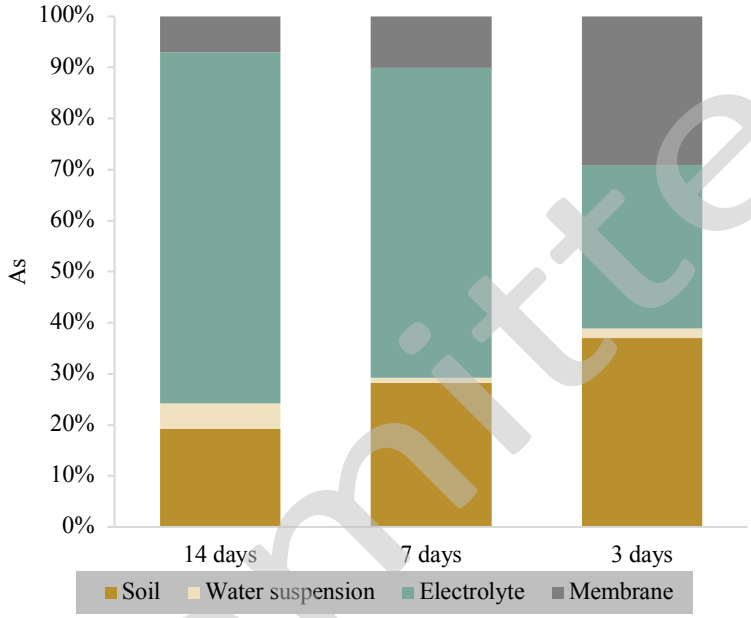

Figure 8 - Distribution of As in different parts of the ED cell for different periods of time (14, 7 and 3 days).

3. Conclusions

The soil from wood preservation industry showed to be highly polluted with As, exceeding 30 times the soil quality criteria in Denmark (20 mg/kg). The EDR of As-contaminated soil showed removals between 400-478 mg As/kg corresponding 50-80% of removal. The pre-treated soil showed higher ($p<0.05$) As concentration in soil but higher removals efficiencies were not achieved being As mainly present after EDR as residual and oxidizable form. The comparison between 14, 7 and 3 days of As EDR showed that As was mostly (approx. 60%) desorbed from soil within the first 3 days, but longer period is required for As to cross the AEM towards anolyte.

Acknowledgements

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PAPER VI *Electrokinetic remediation of oil-contaminated soils in cold climate conditions (in preparation)*

Electrokinetic remediation of oil-contaminated soils in cold climate conditions

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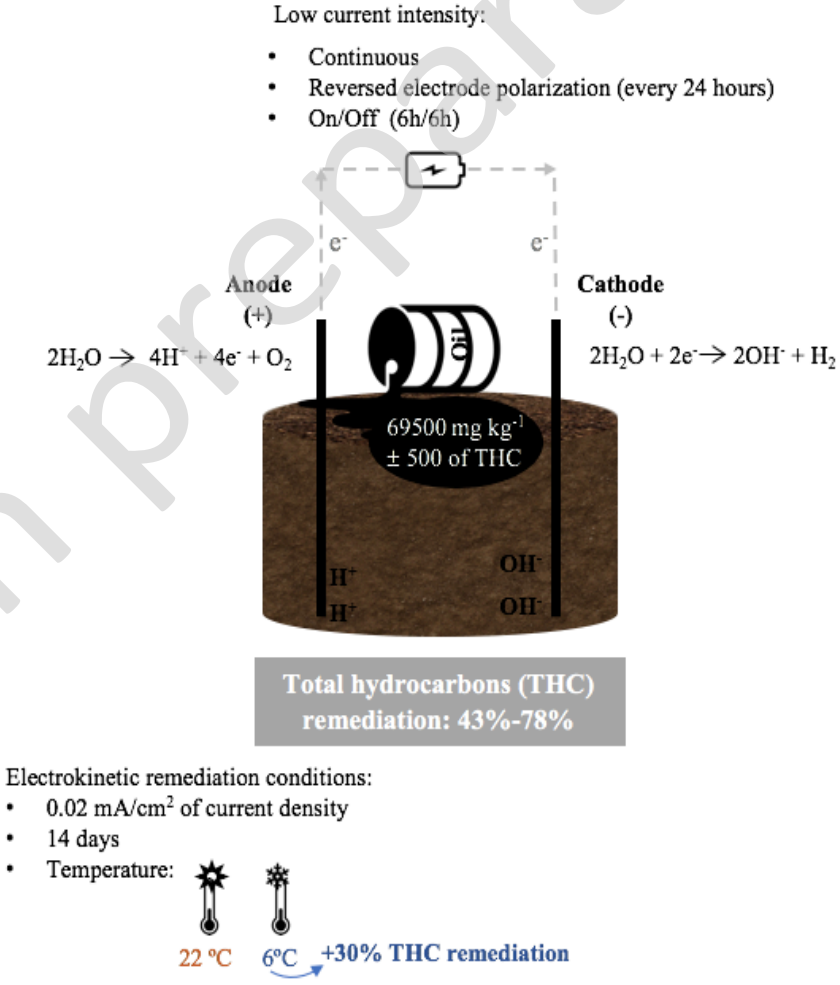
Graphical abstract



Abstract

Oil is one of the most common toxic pollutants of the environment. In cold regions, the persistence and severity of ecological impacts from oil spills can be severe, and therefore, the development of efficient methods of soil remediation from oil is a pressing problem. The present work studies the feasibility of the electrokinetic remediation (EKR) of soil polluted with oil under cold climate conditions. The soil was collected in Sisimiut, Greenland, from a dump site after an oil spill.

The experiments were carried out for 14 days, applying 0.02 mA/cm2 of current density with continuous DC either at room or cold temperature (22 and 6ºC, respectively). Aiming a non-invasive remediation technology, two current strategies: reversed electrode polarization (REP) (every 24 hours) and switching the current On/Off (every 6 hours) were tested. The results were compared with those obtained in a reference experiment in which no remediation actions were taken (no current was applied). The main soil parameters, as well as, elements and metals were monitored before and after EKR.

The soil showed a total petroleum hydrocarbons (THC) concentration of 69 500 mg kg-1 and the levels decreased more than 43% after 14 days of remediation. The effect of the electric field in THC removal was not verified when comparing with the controls (without current), in which volatilization and biodegradation can explain the removals. The EKR was higher under cold temperatures (≈30%) than in room temperature. This may be explained by electrokinetically enhanced biodegradation in cold conditions, as the indigenous microorganisms naturally present in the Sisimiut soil are more adapted to cold temperatures. This hypothesis is supported by the lower removals in the anode compartment, where the continuous electric current showed to have a negative effect, probably due to the heating phenomena. Further studies should be done in order to study the On/Off and REP strategies together: less energy consumption without promoting drastic changes in soil characteristics as pH or heating effect.

Keywords: polar soil, Sisimiut, oil spills, soil pollution, electrokinetic remediation

1. Introduction

Polluted soil is a worldwide problem and in Europe heavy metals and mineral oil are the most frequent soil contaminants (37.3% and 33.7%, respectively) at the investigated sites (1). However, some environments are more sensitive than others. The Arctic environment is very fragile to anthropogenic disturbances due to slow recovery times (2). The Arctic Council has already identified persistent organic pollutants including polyaromatic hydrocarbons (PAH) and other metals Cd, Hg and Pb as priority substances in their Arctic Monitoring and Assessment Programme (AMAP) (3). Some researches pointed out that residents in Arctic regions are exposed to high concentrations of persistent organic pollutants and heavy metals (4,5) and bioaccumulation in the food chain of Arctic mammals was also registered (6). This represent a real threat as hydrocarbons have been reported to be mutagenic and carcinogenic (7).

Human activities in Polar regions are oil dependent and oil spills can happen at any time. In the future, the industry most properly will expand and the probability to get more contaminated sites, which need remediation, could occur. Long exposure to the oil-containing waste may lead to migration of hydrocarbons and other harmful components in the environment, resulting in secondary contamination sites. Knowledge about oil-remediation is therefore an important tool either now or in the future. The physico-chemical properties of oil, such as hydrophobic nature with very low water solubility and high octanol-water partition coefficient, difficult the removal of these compounds as they adsorb tightly to soil organic matter making them less susceptible to biological and chemical degradation (8). Some remediation methods involve the excavation and removal of the polluted soil for treatment using physical or chemical method (9).

From an economic and environmental point of view the in situ decontamination is taking high importance. At the present time, many research efforts have been expanded to find suitable non-invasive methods for the remediation of oil-contaminated soil under cold temperatures, such as bioremediation (10–12). However, the activity of the indigenous hydrocarbon-degrading microbes is limited, likely by a combination of unfavourable conditions including low temperature and moisture, indicating that in situ rates of hydrocarbon degradation are slow (13,14). In this sense, the development of efficient methods for polar soils remediation is a pressing problem and has become a matter of interest.

Electrokinetic remediation (EKR) has been showing to be a promising technology to remediate soil polluted with oil (15). The EKR involves the application of a low intensity direct current (DC) between suitably located electrodes. The electrolysis reactions at the inert electrodes produces protons at the anode and hydroxyl ions at the cathode (16). As a consequence, large pH gradients are caused by the transport of protons and hydroxyl ions generated. Nowadays, the application of this technique alone or combined with other techniques, as for example, with biotechnologies for petroleum hydrocarbons

remediation have been tested (17). Although the soil decontamination by means of the electric field has been demonstrated by some researches, the treatment effectiveness in cold climate conditions from soil is still poorly explored. In this sense, more studies are needed before field application as environmental impacts as yet not been assessed or quantified. The present work discusses the EKR of oil-polluted soil that could work as an effective remediation technology with minimum maintenance and disturbance (soil structure and biological activity) avoiding the rapid diffusion of pollution after an accidental oil spill.

2. Experimental

2.1. Description of the site

The soil samples were collected in Sisimiut (66º56' N, 53º40' W), a city at the west coast of Greenland, approximately 75 km north of the Arctic Circle. This city is the second largest town in Greenland with about 5230 inhabitants (18).

The activities and the life style in Sisimiut have a high oil demand (e.g. transportation and heating). There are many industrial activities located in Sisimiut, being known by the fishing industry, which also increase the oil demand.

The climate of Polar Regions is characterized by short, cold summers and extremely cold winters. The temperatures in Sisimiut range between -16 ºC to 16 ºC. The coldest months are January, February and March, with an average daily temperature for the coldest day of - 16 ºC and - 10 ºC for the average high and low respectively. The warmest months are July and August with average daily low and high temperatures of 6 ºC and 16 ºC for the warmest day respectively. The relative humidity ranges from 49% to 97% in a year, with the driest times in March and the most humidity around August. The shortest day only has one and a half hours of daylight, where the longest day has daylight in 24 hours (19). Putting all of these characteristics together, treating soil pollution might be a challenge due environmental conditions, a very short treatment season, site remoteness and limited local infrastructure.

2.2. Sampling

The soil samples were taken in Sisimiut dump site where the waste is stored to be further burned at the local waste incineration plant. The area is full of used barrels where oil spills could be seen due to leaking (Figure 1). The soil in study was sampled from one of the identified spills in August 2017. The oil-spill could have happened when the oil was being transported or stored. During the sampling, a strong odour of oil products and free phase oil in the surface was observed. The soil was dug up from 0 to 30 cm depth by using a shovel and transported to Denmark in polyethylene bucket. In laboratory,

the soil was carefully homogenized by turning it continuously and stones, bricks, clinker, fibrous roots and so on were picked out.

Figure 1 – The site of the soil sampling in Greenland, Sisimiut (marked with the black dot).

2.3. Electrokinetic experiments

The EK were made in cylindrical boxes (inner Ø=8 cm; height=4 cm) made of Plexiglas was filled with 250 g of soil. The soil was initially weighted, and moisture content was determined. In order to keep the same amount of water in soil during the EKR, the soil was weight once a day in a digital balance, and water was added if needed.

Mixed metals oxide (MMO) coated titanium electrodes with a 3 mm diameter and a 5 cm length (provided by FORCE® Technology, Cathodic Protection) were used and power supply (Hewlett Packard E3612A) maintained a constant DC current. The distance between the two electrodes in EK experiments was 4.5 cm. The experiments lasted 14 days with 0.02 mA/cm2 of current density.

The influence of the cold temperature (6º C, representative temperature of summer at Arctic) in EKR was tested. The experiments were placed inside of the fridge in order to keep the cold temperature constant over the time. For comparison purposes, the same experiment was made at room temperature

(22 ºC). The effect of current in soil characteristics and pollutants removal, was also assessed comparing with reversed electrode polarity (REP) every 24 hours and switching the current On and Off every 6 hours.

At the end of the EKR experiments, each box was divided in two sides: anode and cathode. Oil content, elements and metals, pH, conductivity, organic content and soil morphology were analysed.

2.2. Analytical procedures

2.2.1. Soil characterization

2.2.1.1. General parameters

The main properties of the studied soil were analysed. Water content was calculated as weight loss at 105 °C for 24 h. Organic matter was based on loss of ignition of dried sediment (2.5 g), heated at 550 ºC for an hour. Dried soil (5.0 g) was agitated with KCl (1M, 12.5mL) for an hour and pH were measured using a radiometric analytical electrode, respectively. For conductivity measurements, dried sediment (10.0 g) was agitated with distilled water (50 mL) for an hour and a radiometer analytical electrode was used. Carbonate content was measured by treating dried soil (5.0 g) with HCl (3 M; 20 mL) and the developed CO2 was measured volumetrically in a Scheibler apparatus, calibrated with CaCO3. Chloride content was measured by agitating sediment (10 g) dried at 40 °C with micropore water (40 mL) for 20 h. Solid particles were removed by 0.45 μm vacuum filtration and the chloride concentration was measured by ion chromatography.

2.2.1.2. Determination of metals and major elements

The metals and major elements were measured after digestion: 20.0 mL (1:1) HNO3 added in 1.0 g of dry soil were autoclaved (200 kPa, 120 ºC for 30 minutes). Solid particles were subsequently removed by vacuum filtration through a 0.45 μm filter and the liquid was diluted to 100 mL. The concentrations in the filtrate samples were analysed by Varian 720-ES Ion Chromatography Plasma (ICP-OES). The digestion method is described in Danish Standard (DS) 259 "Determination of metals in water, sludge and sediments - General guidelines for determination by atomic absorption spectrophotometry" (21).

2.2.1.3. Determination of oil in the soil

The soil samples were prepared with an internal standard consisted of three stock solutions with monobrobenzene, o-terphenyl and squalan in pentane. The concentration was 10 000 mg L-1. 1000 µl of each stock solution was added to a 100 ml volumetric flask which was filled with pentane. Hereby the concentrations of the internal standards were 100 mg L-1.

For oil extraction, 60 g of soil was shaken together with 20 ml pentane in a 100 ml redcap glass, the shaking stopped after reaching a liquid suspension (after about 30 seconds of handshaking). 20 ml pentane with internal standard was added to the sample and it was placed at a shaking table at 150 rpm for 24 hours. The organic phase was taken into vial from where further analyses were carried out. The oil content of the polluted soil was determined by gas Chromatography using a Flame Ionization Detector (GC-FID). Pentane controls and blinds were also run randomly in the line sequence. Quantification of initial total hydrocarbons (THC) in the range of C10 to C40 was measured externally at a licensed laboratory following ISO/DIS 16703.

3. Results and discussion

3.1. Soil characteristics

The soil characteristics are summarized in Table 1. Through the grain size distribution, the soil shows a sandy loam texture, which allows a good drainage. The soil shows a neutral pH (7.43) and both low buffer capacity (low content of carbonate, 1.9%) and organic matter (4.4%).

The soil did not show to have lack of nutrients through the P, K, N analysis. The concentration of metals found in the studied soil were below to the limit values in soils in Denmark. However, the presence of Cu (43 mg kg-1), Pb (37 mg kg-1) and Zn (85 mg kg-1) suggests anthropogenic sources. The metals Fe and Al were the most abundant metals found in the soil sample (12702 and 5410 mg kg-1, respectively). This aspect is important as soluble iron compounds, such as Fe2+, are known to play an important role in the degradation of organic compounds by reacting with OH• radicals. Even though, the concentrations of metals are below limit values, their monitoring after EKR is important as the pH changes may promote ions migration.

Regarding THC, the studied soil showed a contamination of 69 500 ± 500 mg kg-1 being 100 mg kg-1 the quality criteria for soil in areas with very sensitive land use in Denmark (22). In terms of the type of the contamination, Figure 2 show the chromatograms obtained for the soil extraction where is possible to see that it contains low- to medium-molecular weight compound mixtures such as diesel fuel.

Table 1 – Soil characteristics

Characteristic	Value	Unit
pH	7.43 ± 0.02	
Conductivity	574 ± 75	µS cm-1
Chloride	3074	mg kg-1
Carbonate	1.9	%
Organic matter	4.4 ± 0	%
Water content	10	%

Grain Size		
Clay	4.40	%
Silt	47.4	%
Sand	48.2	%
Metals and elements		mg kg-1
Al	5410 ± 502	
As	1 ± 0	
Ca	8082 ± 775	
Cd	0 ± 0	
Cr	22 ± 1	
Cu	43 ± 11	
Fe	12702 ± 8998	
K	1820 ± 154	
Mg	3661 ± 279	
Mn	116 ± 9	
Na	613 ± 41	
Ni	26 ± 16	
P	770 ± 54	
Pb	37 ± 5	
S	1653 ± 177	
Zn	85 ± 19	
Oil		mg kg-1
THC	69500 ± 500	

3.2. EKR experiments

3.2.1. General results

Aiming to minimize environment disturbance, it is important to monitor the soil characteristics after EKR. The parameters analysed after the experiments are in Table 2. After application of a continuous electric field, due to the electrolysis of water, the pH became more acidic and alkaline in anode and cathode, about 6.9 and 10.9, respectively. When the polarization was changed, it allowed to prevent the acidification and alkalization in soil because, electrodes are cathode-anode along the 14 days, thus counteracting the acidic and alkaline fronts. For the EKR experiments where the current was switched On/Off, the soil pH only changes in anode side due to oxidation reaction that generates H+ faster than OH- in cathode. This result suggests that the period of Off should be longer than the On (e.g. one day instead of 6 hours) aiming to keep the initial soil pH values.

The initial values of voltage were similar among the experiments and ranged from 17.2 to 23.2 V. Over the time, voltage values had fluctuations, including high levels of voltage were registered. For REP, slight oscillations in the value of the current density corresponding with the daily change in the polarity of the electric field were observed. In general, all changes were a consequence of the changes promoted

in the soil characteristics, which can be explained in terms of an electrical resistance increase of the soil matrix related with the water evaporation, reducing the moisture content and decreasing the soil conductivity.

The changes observed in the conductivity are in agreement with those previously observed for pH. The conductivity increased when continuous current was applied (except in cathode side under cold temperature). This might be associated to the significant increase in the proton and hydroxyl ions concentrations as a consequence of the electrolysis of water. When applying REP, the conductivity did not increase because the acid and basic front are partially balanced. Similar results were showed by Barba et al. 2017 (23).

Regarding organic content, no differences were found between controls (without electric current) and EKR experiments, suggesting that the current did not have any effect in organic matter degradation.

Table 2 – pH, conductivity and organic content and after EKR

Temperature	Type of current applied	Electrode charge	pH	Conductivity (µS cm-1)	Organic content (%)
Room	Continuous	Anode	6.9	489	2.8
		Cathode	10.9	446	2.7
	REP	Anode/cathode	7.7	296	3.0
		Cathode/Anode	8.0	200	2.8
	On/Off	Anode	7.8	376	2.6
		Cathode	10.8	335	2.8
	Control*		8.0	311	2.7
Cold	Continuous	Anode	7.2	455	3.0
		Cathode	10.8	267	2.7
	Control*		7.9	256	3.2

*without electric current

3.2.2. Metals and other elements

Comparing with the initial values (Table 1), the metals and other elements concentration either in anode and cathode did not significantly change (without statistical differences). The values are shown in Table SM. The experimental conditions did not promote the metals and/or nutrients migration in the natural soil matrix, suggesting low mobility and bioavailability. This result can be justified with the soil pH that did not change to very low (pH<4) or high values (pH>11), values that have been reported for the metals to have mobility (24).

3.2.3. Oil remediation

Overall reductions up 75% were observed for THC. The Figure 4 shows the remediation percentages after EKR comparing with the initial soil sample.

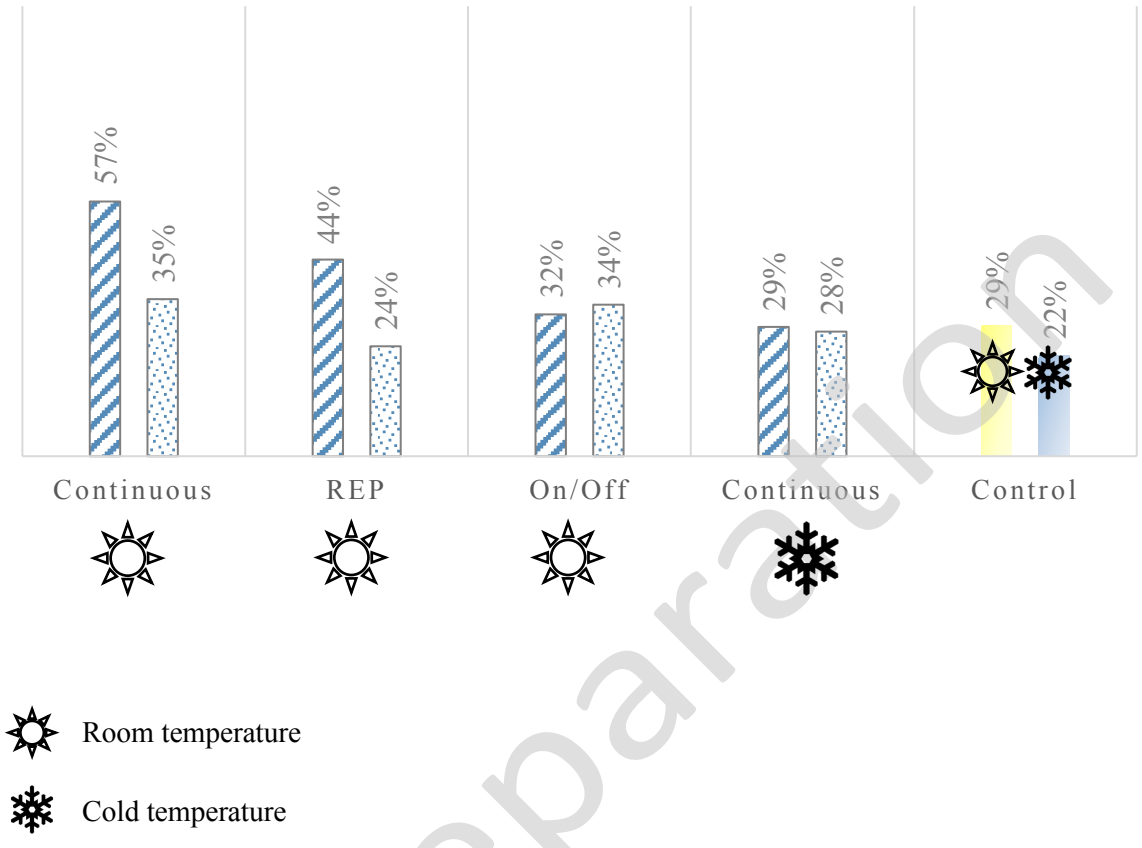


Figure 4 - Presence of THC after EKR (either in anode and cathode) comparing with the initial soil sample value.

Controls (bio and abiotic factors) cold vs. room temperature

Comparing the initial THC concentration with the both controls (without current) it is possible to attribute loss of THC to either bio or abiotic factors. Hydrocarbons odours were felt during the experiments suggesting that volatilization occurred, although air samples were not collected (25). In addition to volatilization, the presence of indigenous cold-adapted microorganisms that persist in contaminated soils showed to have influence in oil degradation and have been study by several authors e.g.(13).

Comparing both controls, at room and cold temperature, slightly differences were found (29% and 22%, respectively). This result suggests that in the tested EKR conditions, temperature did not have influence in oil degradation when current was not applied. The theory about the effect of temperature in the microorganisms is not linear and has been reported to have a great influence in biodegradation (26). In the case of hydrocarbons biodegradation, the temperature directly affects the chemistry of the

compound, as well as, the physiology and diversity of the microbial flora in the contaminated matrix (27). Some studies have demonstrated that hydrocarbons mineralization occurs in soils at low temperatures, however, the rate and perhaps the extent of degradation are higher at elevated temperatures and the bioremediation levels are lower in cold temperatures (12,13). In the other hand, other studies showed the opposite. In Sanscartier et al. (2009) (28), a greenhouse in Canadian high Artic showed an increase of average soil temperatures and extended the treatment season but did not enhance bioremediation. The results confirm that temperature and low moisture content affect biodegradation of HCs in the field. Also, in Pedersen et al. (2017) (29) polychlorinated biphenyl (PCB) removal by electrodialytic process was more efficient at low temperatures, which was attributed to the naturally occurring PCB degrading microbial communities not being adapted to higher temperatures. In the present study, even though no significant differences were found between controls (no current) at different temperatures, when current was applied current some differences were found.

EKR: direct continuous current at cold and room temperature

Comparing with controls, EKR itself did not improve the oil remediation for the tested conditions (Figure 4). However, some differences can be seen among the EKR experiments.

Comparing continuous electric field EKR experiments, between cold and room temperature, more ≈30% was achieved under cold temperature in anode side. The influence of applying an electric field on microbial communities is not completely explored yet. Some studies reported that generally limited effect has been detected (26) and it may even stimulate microbial activity (30). However, chlorine and hydrogen peroxide generated in secondary electrode reactions may inhibit microbial communities adjacent to the electrodes (31). In this sense, the type of current applied can be crucial in the soil remediation by microorganisms, e.g. Ramírez et al. (2015) (32) state that biological treatment could be improved by the use of electrokinetic soil flushing, but only by using the REP.

Current strategy applied in EKR

Among EKR experiments, homogeneous THC remediation was achieved when On/Off was applied (68% and 66% in anode and cathode, respectively) (Figure 4). For continuous electric current and REP, 20% of difference was found between anode and cathode side in terms of THC presence (56% vs. 76% and 44% vs. 24%, respectively). The soil temperature was not measured during the experiments because low current intensity (0.02 mA cm2) was applied and no large changes in soil temperature were expected (33). However, it is important to mention that anode side in these experiments was clearly drier and differences in anode and cathode are probably attributed to the electrical heating as a consequence of the ohmic drops. The application of the electrical current may produce excessive soil heating which would lead to microbial inactivation (23,32). This result can be corroborated comparing the result at room and cold temperature with continuous current (57% vs. 22% in anode at room and cold temperature, respectively). The temperature influences oxygen solubility, which decreases with

increasing temperature, and reduces the metabolic activity of aerobic microorganisms. In REP, differences between anode and cathode were also found, but heating is not expected to be the reason (23). The differences can be attributed to the electroosmotic flow, which was found to decreased with the REP frequency making the microbial distribution in soil not uniform (23). Further studies should optimize the REP strategy testing different periods of time.

In On/Off experiment, the effect of heating in anode side was probably avoided whit the breaks of current. In addition, the Off period allows a less energy expenditure because half of the current was applied. In the present work, the tested conditions did not show the effect of current in oil remediation, but the results are promising. Having in mind the characteristics of the Artic environment, the remediation technology developed must operate under challenging environmental conditions, be easy to operate, have low energy requirements, and have minimal impact on the environment. In addition, it is very important to keep the soil and experimental conditions (such as pH and electrical conductivity) within proper values for microbial life. The REP contributed to make less changes undergone by the soil as a consequence of the electrolysis of water, because they are partially balanced in each polarity reversal. In addition, in theory, the REP favours the homogenization of the system at microscopic scale as it acted as a mixer which put in contact pollutants, microorganisms and nutrients (33). A combination between REP and On/Off could be a strategy to test together in order to optimize the EKR: less energy spend without changes in soil characteristics.

4. Conclusions

Comparing controls (without EK), no differences were found under cold and room temperature; Under a continuous electric field, differences (≈30%) were found between cold and room temperature in anode side; Higher removals were found in cathode side, where cold-adapted microorganisms seem to have influence in oil remediation through the comparison between controls and applied current experiments; Regarding to the different electric current strategies applied, the REP showed not to change the soil pH at both anode and cathode side and switching the current On/Off (6h/6h) seems to be a good practice as both sides (anode and cathode) showed similar oil-remediation. Further studies are needed to find a strategy to make the EKR more efficient and the combination between REP and On/Off seems to be a promising option.

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PAPER VII *Emerging organic contaminants in soil irrigated with effluent: electrokinetics as a remediation strategy (In preparation)*

Emerging organic contaminants in soil irrigated with effluent: electrokinetics as a remediation strategy

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Abstract

The reuse effluent for irrigation is foreseen as a possible strategy to mitigate the pressure on water resources. However, there is the risk of potential accumulation in soil of emerging organic contaminants, as pharmaceuticals and personal care products.

The present work tested the use of direct current, Electrokinetic remediation (EKR) technique for the removal of EOC contaminated soil. The experiments were carried out for 6 days with a low direct current of 2.5 mA. Different current strategies were applied: continuous, reversed electrode polarization (REP), switching the current On and Off and the combination of the last two. The target EOC were selected based on the most detected compounds in effluent and aquatic bodies either in Portugal and some of them in common with Spain and France: a) pharmaceuticals: sulfamethoxazole (antibiotic), diclofenac and ibuprofen (anti-inflammatories), carbamazepine (anticonvulsive), ethinylestradiol (synthetic estrogen), and b) personal care compound: oxybenzophenone (UV-filter).

Among the EOC in study, SFM showed the highest removals (66%-86%) in all EKR experiments and CBMP, EE2 and MBPh the lowest; bioremediation is believed to be the main degradation mechanism for SFM (around 50±8%). The EKR showed to increase the EOC removal in approx.40% when compared with control (without electric current). In general, there was a tendency for lower removals in central compartment and higher removals in cathode side with statistical differences ($p<0.05$) for some EOC. When On/Off + REP was applied more homogenous soil conditions and EOC remediation was achieved.

Keywords: effluent re-use; soil irrigation; Electrokinetic remediation; emerging contaminants

1. Introduction

The water resources are coming increasingly under stress, leading to water scarcity and quality deterioration. This fact has encouraged more active consideration of using alternative water sources as a strategic option to supplement water supplies and protect natural resources. Water reuse and recycling has been identified as one of the five top priorities of the European Innovation Partnership on Water (Laura Alcalde Sanz, Bernd Manfred Gawlik, 2014). In addition, to the need to meet the increasing demands for drinking water supply, and other urban demands (e.g. landscape irrigation, commercial, and industrial needs), there is also increased demand for water for agricultural food production (Laura Alcalde Sanz, Bernd Manfred Gawlik, 2014).

Agriculture is the sector that consumes the most water at the global level, accounting for approximately 70% of total consumption (K. Frenken, V. Gillet, in: AQUASTAT (Ed.), 2012). The reuse of treated wastewater for irrigation is foreseen as a possible strategy to mitigate the pressure on water resources. However, in wastewater treatment plants (WWTP), pharmaceuticals and personal care products (PPCPs) are not completely removed and have been detected in effluent over the years (Verlicchi et al., 2012; Petrie et al., 2014; de Jesus Gaffney et al., 2017). PPCPs, are considered as emerging organic contaminants (EOC) because they still remain unregulated or are currently undergoing a regularization process. In this sense, when effluent is used for agricultural irrigation, some EOC are introduced into the soil simultaneously with the water matrix with the risk of potential accumulation and to migrate in the soil profile, potentially contaminating groundwater (Calderón-Preciado et al., 2011a; Careghini et al., 2015; Kinney et al., 2006; Sui et al., 2015).

Some studies have already reported the presence of PPCPs in plants grown in soils submitted to biosolids application and irrigated with effluent. Malchi et al. (2014) (Malchi et al., 2014) found 14 different PPCPs, such as carbamazepine, caffeine, clofibric acid, diclofenac, ibuprofen, ketoprofen and naproxen in carrots and sweet potatoes irrigated with treated wastewater. Calderón-Preciado et al. (2011) (Calderón-Preciado et al., 2011b) also reported the occurrence of a wide range PPCPs e.g. salicylic acid, caffeine, ibuprofen, methyl dihydrojasmonate and galaxolide, in apple tree leafs and alfalfa with concentrations of 0.016-16.9 ng g-1 (wet weight). Wu et al. (2015) (Wu et al., 2015) detected caffeine, carbamazepine, naproxen and triclosan in eight vegetables, with a total PPCPs concentration in the range of 0.01-3.87 ng g-1 (dry weight). (Christou et al., 2017) reported that DCF displayed the highest fruit concentration (11.63 µg kg-1) throughout their study (as a result of prolonged WW irrigation), followed by SFM (5.26 mg kg-1).

The adverse effects of these EOC still unclear. However, some studies have been conducted to investigate the environmental risk of PPCPs by comparing the difference between predicted concentration and measured concentration or predicting the adverse effect concentration with regard to specific organisms. It has been shown that continuous exposure to low, subtoxic concentrations of

certain PPCPs can cause unexpected consequences and unintended effects on non-target species and induce undesirable effects on humans and ecosystems. Previous works have suggested that environmental exposure to PPCPs is inducing the formation of antibiotic-resistance in bacteria, which may represent a major human health risk associated with antimicrobial resistance (Piña et al., 2018). Also, chronic impacts on biodiversity including to alter the metabolism, development, and/or reproduction of fish (Meador et al., 2016). Some other EOC effects are summarized in (Gogoi et al., 2018).

Because of all of these reasons, there the need to study technologies that are able to clean the contaminated soil. The EKR involves the application of a low intensity direct current (DC) between suitably located electrodes as the ‘‘cleaning agent”. The electrolysis reactions at the inert electrodes produces protons at the anode and hydroxyl ions at the cathode (Acar, Y. B., & Alshawabkeh, 1993). As a consequence, large pH gradients are caused by the transport of protons and hydroxyl ions generated. The electric potential induces the migration of contaminants toward the electrode by two primary transport processes, namely electromigration, electro-osmosis and electrophoresis (Virkutyte et al., 2002). EKR have already demonstrated to have potential to remove different types of contaminants, including PPCPs (Guedes et al., 2014b) from several contaminated matrices alone and/or coupled with other technologies (Couto et al., 2015). Electrodes polarity reversal has been reported as effective at maintaining uniform pH conditions (Harbottle et al., 2009) and enhancing mixing of substances in situ by alternating the migration path (Mena et al., 2016). The present work is focus on the EOC removal from soil by EKR that could work as an effective ree technology with minimum maintenance and disturbance (soil structure and biological activity) avoiding the rapid diffusion of EOC present in effluent after soil irrigation. The target EOC were selected based on the most detected compounds in effluent and aquatic bodies either in Portugal and four EOC in common with Spain and France: a) pharmaceuticals: sulfamethoxazole (antibiotic), diclofenac and ibuprofen (anti-inflammatories), carbamazepine (anticonvulsive), ethinylestradiol (synthetic estrogen), and b) personal care compound also present: oxybenzophenone (UV filter). These compounds have a different range of physical and chemical characteristics: $0.89 < \text{Log Kow} < 4.51$; $4.15 < \text{pKa} < 13.9$ and $2.37 < \text{solubility} < 610$ mg L-1 (Table 1). The fate of PPCPs is rarely investigated during currently applied effluent irrigation, with few studies reporting the effect of reclaimed water matrix on PPCPs fate in soils (Chen et al., 2013; Dodgen and Zheng, 2016; Kinney et al., 2006; Ternes et al., 2007), but no studies were found about remediation technologies after soil irrigation with contaminated effluent to assesses EOC mitigation, in order to avoid the potential risks.

Table 1 - Information of target EOC.

Emerging Organic Contaminant (EOC)	Formula	MW (g/mol)	Log Kow a	pKa b	Solubility (mg/L)	H (atm-m³ /mole)	Category
Sulfamethoxazole (SFM)	C10H11N3O3S	253.279	0.89	5.7	610 f	6.4x10-13	Antibiotic
Carbamazepine (CBMP)	C15H12N2O	236.274	2.45	13.9	18 d	1.1x10-10	Anticonvulsive
17α-ethinylestradiol (EE2)	C20H24O2	296.40	3.67	10.3	11.3 e	7.94x10-12	Estrogen
Diclofenac (DCF)	C14H11Cl2NO2	296.147	4.51	4.15	2.37 d	4.73x10-12	Anti-inflammatory
Oxybenzone (MBPh)	C14H12O3	228.25	3.82	7.56	69 d	1.5x10-8	UV filter
Ibuprofen (IBU)	C13H18O2	206.19	3.97	4.91	21 d	1.5x10-7	Anti-inflammatory

References:
http://pubchem.ncbi.nlm.nih.gov
https://chem.nlm.nih.gov
Legend:
MW: molecular weight
pKa: dissociation constant
Log Kow: Octanol water partition coefficient
H: Henry's law constant

2. Materials and methods

2.1. Standards and chemicals

All ssolvents, HPLC grade, were from Merck (Darmstadt, Germany) and Sigma–Aldrich (Steinheim, Germany). Deionized water waswas purified with a Milli-Q plus system from Millipore (Bedford, MA, USA). All standardsstandards were purchased from Sigma-Aldrich (Steinheim, Germany) with high purity grade (>97%).

All pharmaceutical standards used were of high

purity grade (>90%).

Individual stock solutions for calibration purposes were prepared by dissolving each compound in MeOH at a concentration of 4000 mg L-1 and stored at -18 ºC.

2.2. Soil sampling and characterization

The soil was sampled from Paul de Magos, Salvaterra de Magos, Portugal, at 0-20 cm depth, corresponds to a Fluvisol (World Reference Base for Soil), and its characteristics are presented in Table 2. The soil has a silty loam texture (with 53.4% clay), high mineral and organic colloid contents, which leads to a high cation exchange capacity.

Table 2 - Characteristics of the soil used in the experiments

Parameters	Value
Sand (%)	19.7
Silt (%)	26.9
Clay (%)	53.4
pH(H2O)	6.23
Conductivity (mS cm-1)	0.28
Total carbon (g kg-1)	24.6
Organic content (g kg-1)	42.4
Cation exchange capacity (cmol(+) kg-1)	22.7
Exchangable cations (cmol(+) kg-1)	
Ca2+	11.3
Mg2+	5.7
K+	0.5
Na+	1.2
Sum of exchangable cations (cmol(+) kg-1)	18.7

2.3. Effluent sampling and characterization

Effluent samples were collected at a WWTP from Simarsul located in Quinta do Conde, Sesimbra, Portugal (38º34'13" N, 9º2'7" W). The WWTP has infrastructures with capacity to treat 19,300 m3/day of urban wastewater, corresponding to about 94,000 equivalent inhabitants. The treated wastewater is discharged into Tagus river. The WWTP has an aerobic reactor of suspended biomass to allow the biological treatment of wastewater. The effluent from this reactor goes to the secondary settling tank for phase separation where liquid samples were collected. The effluent samples were taken in June and July. The initial effluent characterization was performed by the WWTP and the main physicochemical characteristics of the effluent can be seen in Table 3. All samples were transported in a cooling box from the WWTP to the laboratory and kept at ±4 C in dark conditions.

Table 3 – Effluent characterization

Effluent sample number	*Effluent 1*	*Effluent 2*
Date of sampling	21.06.2018	19.07.2018
Color	Pale yellow	Pale yellow
Odor	Very weak	Very weak
pH	8.00	8.03
Conductivity (mS cm-1)	1.12	1.23
Total phosphorus – P (mg L-1)	0.84	2.50
Total chloride - Cl- (mg L-1)	< 0.10	< 0.10
Total suspended solids - TSS (mg L-1)	30	< 10
Chemical oxygen demand - COD (mg O2 L-1)	75	30
5-day biochemical oxygen demand - BOD5 (mg O2 L-1)	18	< 3

2.4. Experimental setup and design

The experiments were carried out in a simulated microcosm assembled in a parallelepiped-shaped glass container with round corners (140 x 140 x 50 mm; Figure 2A) externally covered with aluminum foil (to prevent light exposure in depth). Two metal mixed oxide mesh electrodes (IrO2/RuO2-Ti; 90 x 20 x 1 mm; Figure 2B) were placed at microcosms lateral sections, 50 mm apart from each other. applying 2.5 mA of current intensity.

For each experiment, the microcosm was filled 300 g of soil and irrigated with spiked effluent (100 mL; 15 mg L-1 of each EOC) and left for 3 days at 56 ºC to simulate contamination aging while minimizing biological activity. Prior beginning experiments, soil sub-samples were collected and analyzed for EOCs, moisture content, pH and conductivity. The concentration of EOC detected after these 3 days was considered as the initial for comparison purposes with EKR.

The EKR experiments (duplicates) were carried with a DC of 2.5 mA (power supply, Agilent E3612A) during 6 days at room temperature (22 ºC), without direct light exposure. Four types of current strategies were applied in the experiments (Figure 1):

continuous current (CC): run with continuous DC application;

On/Off: DCDC was switched off during day 3 (24 h) and turned back on at day 4;

reversed electrode polarization (REP): electrodes polarization was reversed at day 3 for 24h;

On/Off + REP: DC was switched off during day 3 (24 h) and turned back on with a simultaneous polarization reversion at day 4.

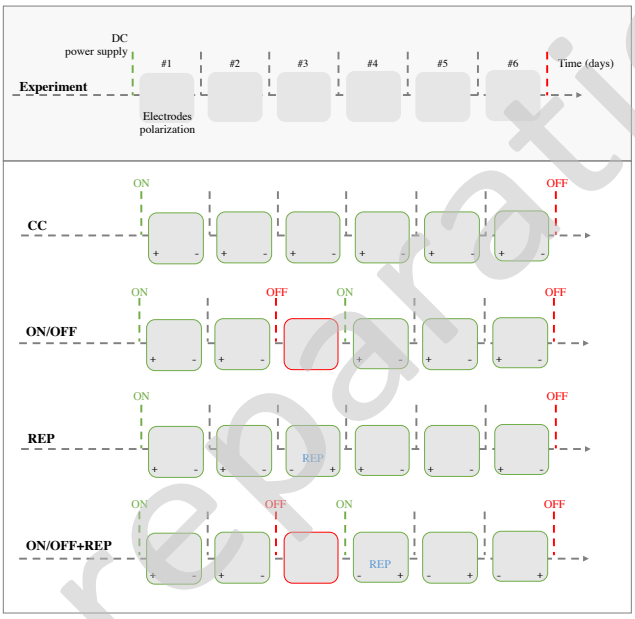


Figure 1 – Schematic representation of the current strategies adopted for the Electrokinetic soil remediation experiments.

Along the experiments, the parameters: current intensity, voltage drop between the electrodes and soil temperature were continuously monitored and microcosms were daily irrigated to keep moisture content somewhat constant (soil was weight once a day and deionized water added till initial weigh). At the end of the EKR experiments, soil layer was carefully removed and segmented into three sections: anode, central and cathode, which were immediately processed and analyzed for EOC, soil moisture, pH and conductivity.

In parallel, control experiments were performed (duplicate) with no current applied for the 6 days (i.e. natural attenuation control).

2.5. Analytical procedures

2.5.1. General parameters

The water content of the soil was measured as the weight loss after 24h at 105 ºC. The pH and conductivity were measured using a soil deionised water ratio of 1:2.5 (w:v), stirred for 1 h, using a pH meter (Metrohm-Solitrode with Pt1000) and a conductivity meter (Horiba-LAQUAtwin), respectively.

2.5.2. EOCs extraction

2.5.2.1. Soil

The levels of each EOC in the soil sections (duplicate) were determined using a QuEChERS (quick, easy, cheap, effective, rugged, and safe) method (adapted from Pinto et al., 2010). In brief, each 2.5 g of soil were mixed with 1.5 mL of deionised water (vortex: ca. 15 s); then with 2.5 mL of acetonitrile (vortex: 1 min); and finally, with 1 g MgSO4 (mixed manually then vortex: 30 s). The supernatant (organic phase) was recovered by centrifugation (5,000 rpm, 5 min), then filtrated through 0.45 µm PTFE syringes filters (previously passed through acetonitrile) and conserved at −20 ºC until analysis.

2.5.2.2. Effluent

The effluent samples were pre-cleaned/concentrated by solid phase extraction (SPE), Oasis HLB 500 mg (Waters; Saint-Quentin En Yvelines Cedex, France), andand an SPE manifold connected to a vacuum pump. The cartridges were conditioned by washing with 3 × 6 mL of MeOH, followed by re-equilibrium with 3x6 mL of Milli-Q water. For organic compounds enrichment, the samples were acidified to pH 2 before extraction, using nitric acid. The aqueous samples (200 mL) were passed through the cartridge at a flow-rate of approx. 10 mL/min. After, cartridges were dried for approx. 2 min by vacuum. The extracts were eluted with 2 × 6 mL of MeOH and, whenever needed, concentrated under a gentle stream of nitrogen. Samples were transferred to a vial and kept at 5ºC until analysis. Before analysis, each sample was filtrated through FILTER-LAB® polytetrafluoroethylene (PTFE) syringes filters (pore size of 0.45 µµm), previously passed through methanol and transferred to a vial.

Before EKR experiments, the effluent samples were extracted and analyzed before soil irrigation and none the compounds under study were detected.

2.5.3. EOC analysis

The EOCs quantification was performed by high performance liquid chromatography with a diode array and fluorescence detectors (HPLC–DAD-FLD). HPLC analysis was performed on 1260 Infinity II LC Systems (Agilent Technologies, USA) equipped with 1260 Infinity II Quaternary Pump (G7111B), a 1260 vial sampler (G7129A), a diode array detector (G1315B) and a fluorescence detector (G1321A)

both from Agilent 1100 Series. The UV wavelength was set to scan from 200 to 500 nm and the fluorescence to 220 nm of excitation and 290 nm of emission.

The separation of the analytes was carried out using a Chromolith High Resolution RP-18 column with 100mm x 4.6mm from Merck (Darmstadt, Germany) connected to an Onyx SecurityGuard C18 cartridges (5mm×4.6mm) from Phenomenex (Torrance, USA). The oven was set to 36 °C. The HPLC runs were performed at a constant flow of 0.5 mL/min, in gradient mode. The two eluents used were composed of a given percentage of Mili-Q water/ACN/Formic acid (eluent A: 94.5/5/0.5; eluent B: 5/94.5/0.5). The formic acid was diluted 50% in water. All eluents were filtered before use by Nylon 66 membranes (pore size of 0.45 µm; Bellefonte, PA, USA). The gradient run was set to: 3min 5% B, after 95% B until 20 min, then 97% B from 20-22 min, where it was held constant until 25 min, then to 95% A until 27 min.

Immediately prior analysis, 200 µL of sample extracts were mixed with 100 µL of eluent A (2:1) in a vial with insert. The target compounds were quantitatively measured at: 275 nm for CAF; 282 nm for SMX and TCS; and 220 nm for IBF. All operations and data analysis were processed using the LC OpenLab software. Repeatability presented a coefficient of variation between 8 and 29% whereas intermediate precision was between 5 and 16%. Methods limits of detection and quantification (LD and LQ, respectively) can be found in SM.

2.6. Statistical analysis

Statistically significant differences among samples for 5% level of significance (95% confidence interval, $p<0.05$) were evaluated through one-Way ANOVA Tukey's multiple comparisons test, using GraphPad Prism software (version prism 7).

3. Resuts and discussion

3.1. General results

pH

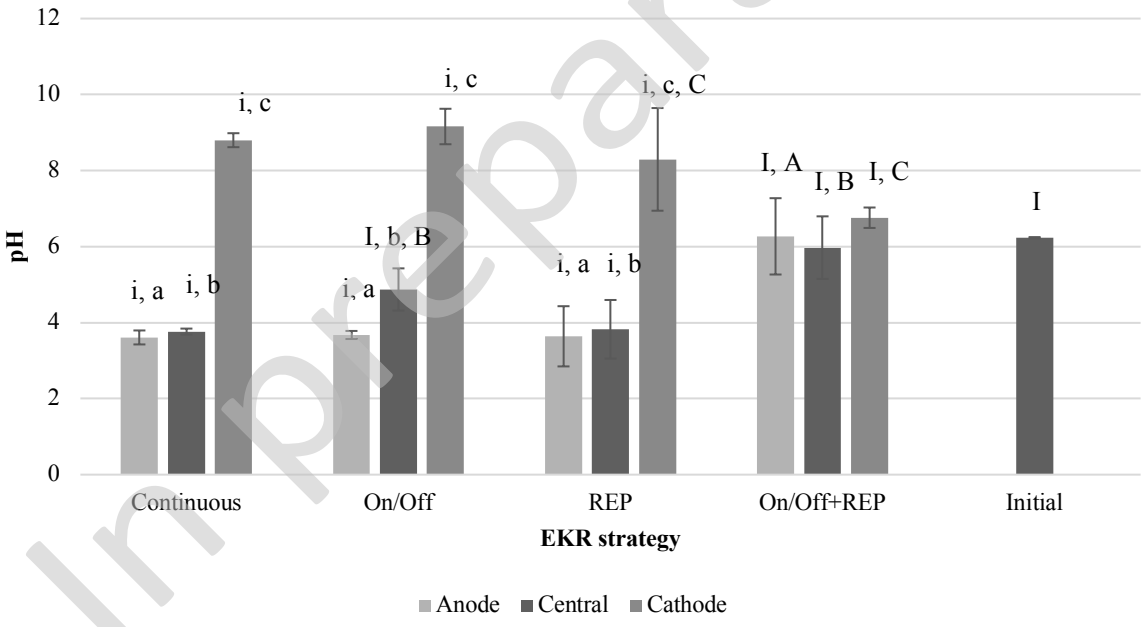
The soil presented an initial pH of 6.23 ± 0.02 and after the control experiment (7 days without electric current) soil pH was 6.48 ± 0.04 without statistical differences ($p>0.05$). After application of a DC field it is expected that, due to the electrolysis of water that generates H+ and OH- ions, soil pH changes to acidic and alkaline in anode and cathode, respectively. All the EKR experiments showed significant differences ($p<0.05$) when comparing with soil initial pH (Figure 3), with the exception of:

soil in the central compartment (pH= 4.9 ± 0.6; $p>0.05$) when the current was switched Off for 1 day (On/Off experiment);

all soil sections (central, anode and cathode) in the On/Off + REP system.

These results show that switching Off the current for 24h does not significantly ($p<0.05$) affect pH changes comparing to a continuous current application (CC). In both cases, anode and cathode soil pH changed to acidic and alkaline, respectively, being statistically different from initial soil pH ($p<0.05$). The electro-polarization reversion for 24h, did not present significant advantages on maintaining soil pH, with all soil sections pH being different from the initial value ($p<0.05$). However, when combined the On/Off for 24h followed by electrodes polarization reversion for a longer period of time, 72h, pH remained somewhat similar between soil sections (anode, central and cathode; between (6.0 and 6.8), although it is still different from soil initial pH ($p<0.05$)

The acidification of the soil in the central compartment is expected when REP is not applied, being attribute to the effective ionic mobility of H+ that is about 1.8 times higher that of OH- and, under an electric field, the acid generated at the anode advances across the soil column, neutralizing the base (Acar, Y. B., & Alshawabkeh, 1993). The soil under study presented a low carbonate content, which according with the literature is related with low buffer capacity, not being able to effectively counteract the H+ ions generated at the anode (Reddy et al., 1997).



Statistical analysis: capital letters means NO statically differences ($p<0.05$):

I: significant statistical differences between initial soil pH and the different compartments for all the experiments

A: significant statistical differences for anode compartment between experiments

B: significant statistical differences for central compartment between experiments

C: significant statistical differences for cathode compartment between experiments

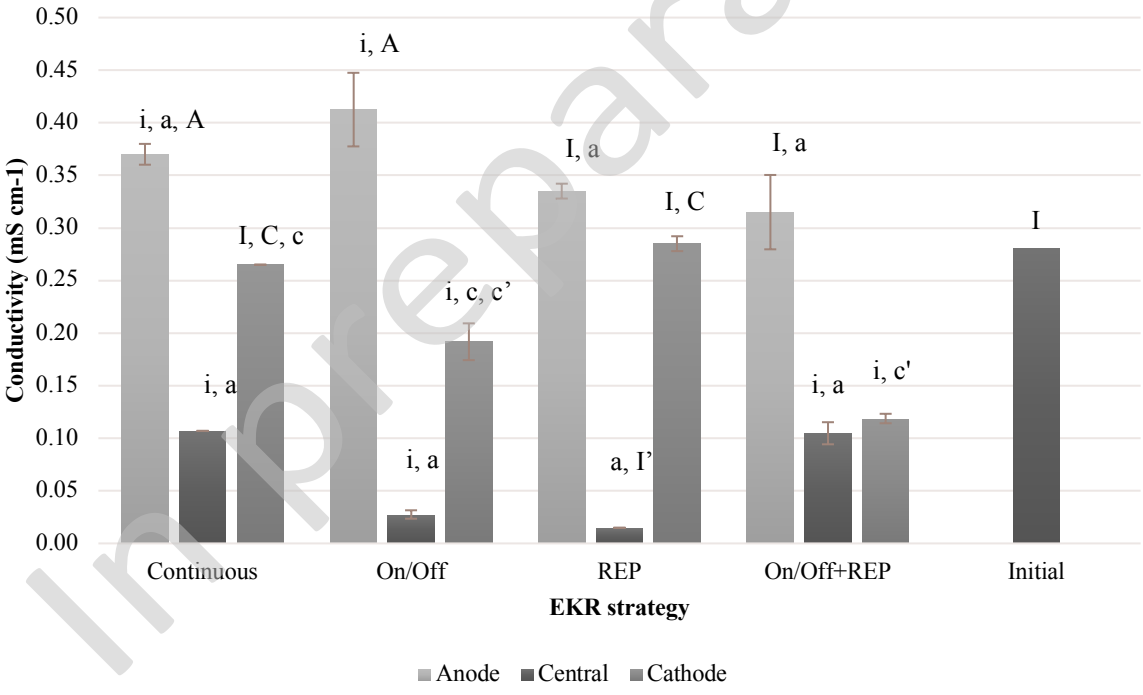
Figure 2 - pH values for the different EKR strategies applied in soil.

Conductivity

Soil initial conductivity was 0.28 ± 0.0 mS cm-1 and 7 days after irrigating with spiked effluent it slightly decreased to 0.19 ± 0.02 mS cm-1 (without electric current; Figure 4). Comparing with the initial value, the conductivity decreased around ten times ($p<0.05$) in the central compartment for all the experiments. This decrease is attributed to ions migration, imposed by the electric field, from the central to the electrodes soil sections. No differences ($p>0.05$) were found between the central compartment of the distinct EKR experiments.

Between anode and cathode, all the experiments (except On/Off + REP) showed significant differences ($p<<0.05$) comparing with the initial value. In the On/Off + REP the production of ions were balanced by the electro-polarization reversion for longer periods (for each electrode section the electrode was anode for 48h and cathode for 72h.

In the anode section the conductivity increased ($p<0.05$) for CC and On/Off experiments due to hydroxide ions generation. When the DC field was switched Off for 24 h (On/off and On/Off+REP experiments) a conductivity decrease in the cathode section was observed ($p<0.05$.).



Statistical analysis: capital letters means NO statically differences ($p<0.05$):

I: significant statistical differences between initial soil pH and the different compartments for all the experiments

A: significant statistical differences for anode compartment between experiments

B: significant statistical differences for central compartment between experiments

C: significant statistical differences for cathode compartment between experiments

Figure 3 - Soil conductivity for EKR experiments.

Voltage

The voltage drop between the electrodes ranged from 3.3 ± 0.6 to 27.6 ± 0.7. The voltage values had fluctuations along the time, in which the high levels of voltage were registered. These changes are a consequence of an electrical resistance increase, mainly attributed to the water evaporation. The water evaporation during EK can be a consequence of evaporation caused by room temperature (kept at 22 ºC) and ohmic heating caused by the soil acting as an electrical resistor when an electric current is passed through it. Even though the soil temperature did not increase significantly ($p>0.05$) and the moisture was kept somewhat constant along the time, there was a slight moisture content decrease between daily irrigations (20 mL of deionized water was added daily). This small variations indicate water evaporation which in turns increases electrical resistance (Page, M.M., Page, C.L., 2002) and, consequently, the increased voltage drop.

3.2. EOC remediation

The amount of contaminants not detected in soil after EKR in relation to the initial amount determined in the soil after aging (spiking followed by 3 days at 5ºC) was considered as remediated. Calculations were performed according to Eq. (1).

$$Remediation\ (\%) = \left(1 - \frac{EOC\ (mg\ kg^{-1})\ in\ soil\ after\ EKR}{Initial\ EOC\ (mg\ kg^{-1})\ in\ soil}\right) \times 100 \qquad \text{Eq. (1)}$$

Table 4 shows the amount of EOC that remained in the soil after the experiments (not remediated).

Natural attenuation

A study of any contaminated site must first be performed to assesses if natural attenuation phenomena make a positive input in compounds removal. The controls (without applied electric current) showed that all compounds suffered natural attenuation in 6 days being the highest removal obtained for the antibiotic SFM (49±8%) followed by DCF ≈ IBF (46%) > EE2 ≈ MBPH ≈ CBMP. (approx. 30%). EOC volatilization from soil is not expected to due to the estimated Henry's Law constant. The photodegradation is not considered as the experiments were carried out indoor and the microcosms were covered in order to simulate the substrate. The influence of the indigenous microorganisms natural present in soil and in this case, also introduced by irrigation with effluent, might justify the removals for the controls in 6 days.

The effect of soil sterilization showed to prolong the presence of PPCPs in soil, indicating that microbial activity played an important role in the degradation of these chemicals in soils (Xu et al., 2009). The biodegradation of PPCPs by microbial activity was already reported for several authors in soils and also in sediments e.g. (Conkle et al., 2012; Foolad et al., 2016; Lin and Gan, 2011; Thelusmond et al., 2018). Also, the irrigation with effluent also introduced nutrients, as phosphorus, particulate and dissolved

organic matter (DOM) in soil. This might have impacts on the overall EOC remediation. (Annamalai et al., 2014) reported that PPCPs persistence decreased due to increased microbial activity, because DOM can serve as substrate for microorganisms.

Besides the microbial activity, the irrigation with influence have other potential implications on PPCP persistence. The dissolved matter from reclaimed water was found to significantly increase the half-life of several PPCPs, while particulate matter was found to significantly decrease half-life of the same PPCPs (Dodgen and Zheng, 2016).

Effect of the electric field

When CC was applied, EOC concentration in the central soil section reached values between 44 and 127% (SFM and IBF respectively) in relation to initial soil concentration (Table 3.11). DCF and IBF showed the highest concentration in central compartment. This fact might be an indication that EOC migrated towards the electrode. Similarly, to CC experiment, IBF also presented a concentration above 100% in the central soil section for REP (+14%; 3.14), with DCF concentration remaining around 100%.

Excluding SFM, the other EOC have 2.45 < Log Kow < 4.5, which makes them easily adsorbed onto the soil organic matter than SFM (Log Kow = 0.89). In terms of Log Kow of the EOC follow the order: SFM (0.89) > CBMP (2.45) > BPA (3.32) > EE2 (3.67) > MBPh (3.82) > IBF (3.97) > DCF (4.51). There have been many attempts to correlate remediation with Kd and Log Kow of compounds (Verlicchi and Zambello, 2015). Higher Log Kow imply a higer Kd (solid liquid partition coefficient). This can justify the higher accumulation of IBF and DCF. These two compounds exist almost entirely in the ionized form at pH values of 5 to 9 (extremes depending on electrodes positioning), (pKa = 4.91 and 4.15, IBF and DCF). Being as an anion form they will migrate to the anode side. However, the pH changes in soil profile when approaching the anode side will make these compounds accumulating in central section as they are less mobile and strongly sorb to soil particles (Yu et al., 2013). The distribution of EOC between aqueous and solid phase is dependent of sorption mechanisms, which in turn can also affect their degradation and mobilization during the ED process.

Current strategies

Comparing all EKR strategies applied, the results show differences among the EOC removals (Table 2). When the DC was switched Off for 24 h, the degradation in the central compartment improved with statistical differences ($p<0.05$) for DCF and IBF comparing with CC. Comparing the three soil sections in the On/Off system, the anode section presented lower concentration for CBMP, EE2 and MBPH, whereas the cathode had lower values of SFM, DCF, IBF (with statistical differences between anode and cathode for CBMP, (IBU; $p<0.05$). These differences can be justified with the fact that in cathode, IBF (pKa = 4.91) and DCF (4.15) have a pKa < pH of the soil in cathode. The same in central compartment when the current was switched Off. As these compounds are present in an ionizable form,

solubility increase and electromigration towards the anode compartment increase. But when approaching the anode, the pH changes over the soil profile, makes IBF and DCF to preferential accumulate in central compartment. Contrary, CBMP, BPA, EE2 and MBPh have a higher pKa than soil pH, which make them more mobile to migrate by DC. Besides the pH control with On/Off, that showed to positively enhance IBF and DCF removal from soil compartment (Cameselle and Reddy, 2013) reported that the Off period during a continuous electric field gives time for the transfer from soil particles to soil moisture being then pulsed with switching On the current.

Regarding REP, a continuous current was maintained for over the 6 days, but the electrodes polarization shifted at day 3 for 24h. It is reported that REP favors the homogenization of the system as it acts as a mixer by putting in contact pollutants, microorganisms and nutrients (Mena et al., 2016). For REP the electroosmotic flow goes to both directions and an homogenous mobilization of EOC was expected for both directions. However, the limitation on EOC mobilization might be attributed to the unavoidable soil moisture changes during the day that limit the electroosmosis and diffusion transport processes of the EOC being considered as the key transport phenomenon for the removal of organic contaminants in soils, sludge and sediments (Cameselle and Reddy, 2012). The large number of variables that affect the electro-osmotic flow and their spatial and temporal variations under applied electric potential make it highly variable and very difficult to predict (Cameselle and Reddy, 2012). Besides the low moisture negatively affect the EK process due to the low soil conductivity, the soil moisture level is considered very important for the proper functioning of the biological process, as low soil moisture can also negatively affect the biological communities (Mena et al., 2016).

By combining the On/Off + REP, removals remained similar to the other remediation strategies except for IBF in the central section (52±18% removal) with statistical differences comparing with CC and REP. The combination of periodic electric current with reversed electric polarizations seems to be a promising EK current strategy as it has potential to combine the advantages of both.

This study shows that once introduced in soil through effluent irrigation, 20%-100% of the studied EOC are present in the soil after 6 days of treatment, posing a potentially risk to the environment and human health. Some studies have already reported the presence of EOC in groundwater, which means that they can be mobile and leach through soil profile (Sui et al., 2015; Yu et al., 2013) due to the heavy rain and irrigation. (García-Santiago et al., 2017) highlight that special attention has to be paid to soil properties, since some persistent compounds with a high mobility in soil, like CBMP, may behave differently depending on soil texture and organic matter content. In some studies, CBMP was found to be accumulated in topsoil layers (Paz et al., 2016) and was rated as low according to its leaching potential (Oppel et al., 2004). Nevertheless, (Gielen et al., 2009) found that CBMP leached consistently below the top 0.9 m, while (Ternes et al., 2007) detected it in lysimeter effluents and groundwater samples from agricultural fields irrigated with treated wastewater for more than 45 years.

It should be pointed out that some samples had higher standard deviations (SD), which influence the statistical analysis and therefore the comparison between current strategies and EOC removals. The high deviations obtained may be associated with EOCs compounds distribution along the two experimental duplicates as the microcosm were manually prepared by (i) putting 300 g of spiked soil in the cell and manual pressing to even the soil height along the microcosms and (ii) manual irrigation. Thus, it was accepted that there would be some variability in the results. Both factors may influence soil compaction and water distribution within the two different microcosms (n=2) which in turn may have influenced the EOC mobilizations/distribution in the soil column through electro-migration and -osmosis and diffusion. Also, no physical separation was used between soil sections, which may have led to a misdistribution when dividing the soil sections in the duplicate microcosms, thus influencing the SD.

Table 4 - Presence (%) of EOC after soil EKR (n=2).

		Emerging Organic Contaminants											
		SFM		CBMP		EE2		DCF		IBF		MBPh	
EKR strategy		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Continuous	anode	26 B	14	69 b	11	67 b	11	77 a, b	17	89 a, b	16	70 b	8
	central	44 B	10	82 b	2	87 b	5	110 A, b	7	127 A, b	35	86 b	5
	cathode	19 B	7	77 b	5	71 b	4	58 a	5	45 a	9	60	2
On/Off	anode	20 B	7	57	15	61 b	11	64 a	12	94 A, b	16	59	10
	central	26 B	19	84 b	23	76 b	12	84 a, b	52	73 A, a, b	47	72	17
	cathode	14 B	4	84 b	3	79 b	7	36 a, B	9	44 a	12	77 b	6
REP	anode/cathode	14 B	5	51 b	4	58 b	0	62 a	3	81 a. b	7	54	2
	Central	34 B	2	70	2	73	5	101 A. b	6	114 A. b	21	75	1
	cathode/anode	19 B	7	77 b	5	71b	4	58 a	5	45 a	9	60	2
On/Off + REP	anode/cathode	19 B	17	69 b	4	63 b	8	48 a	26	48 a	18	61	3
	Central	44 B	19	96 b	6	80	9	98 A, b	6	60 a	26	83	1
	cathode/anode	21	5	60	23	60	26	47 a	8	64 a	25	56	29
Control		51	8	77	6	71	4	64 a	4	64 a	2	71	1

Legend:
Red values mean the higher value among soil section (anode, central and cathode); The values in bold and red highlight the values higher than 100%;
The capital letter 'B' means statistical differences ($p<0.05$) comparing the contaminants presence for each treatment and each section (anode, central, cathode);
The capital letter 'A' means statistical differences ($p<0.05$) for each EOC in the different compartments between the EKR strategies;
Note: for SFM, CBMP, EE2 and MBPh statistical differences were not found for each compound among treatments in the different compartments (anode, central, cathode).

Future research directions

Overall, this study provides insights about the extension of the EOC remediation in soil by EKR after effluent irrigation.

It is reported that the presence of an electric field, if suitably applied, may enhance contaminant biodegradation in unsaturated soils (Gill et al., 2014; Harbottle et al., 2009; Li et al., 2012). Further studies should focus on coupling the remediation technologies: bio and EK remediation for PPCPs removal from soil.

Cycles of effluent irrigation should be tested to assesses if EKR is able to mitigate the presence of these compounds, horizontally or vertically, after several irrigation cycles;

Also, since effluent vary greatly in biological-physical-chemical properties, a systematic understanding of the interactions between water matrix components and PPCPs is necessary.

1. Conclusions

The EKR improved the EOC remediation in approx. 40% when comparing with control (without electric current) and to be a promising technology to be applied in soils contaminated by effluent irrigation; In general, there was a tendency for higher removals in cathode side with statistically differences ($p<0.05$) for some EOC; The central compartment showed higher EOC concentrations meaning that contaminants were mobilized but probably due to the soil characteristics changes (e.g. pH) it accumulated in soil; The combination of On/Off with REP showed to be the most suitable strategy as did not change the soil characteristics in terms of pH and conductivity and more homogenous remediation of the EOC was achieved. Among the emerging organic contaminants in study, SFM showed the higher removals (66%-86%) in all EKR experiments however, mainly due natural attenuation (50±8%); bioremediation is believed to be the main degradation mechanism for this compound in the tested conditions.

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IP protection material *Electrochemical degradation of emerging organic contaminants from effluent: electro-catalytic materials and design influence (in preparation)*

Electrochemical degradation of emerging organic contaminants from effluent: electro-catalytic materials and design influence

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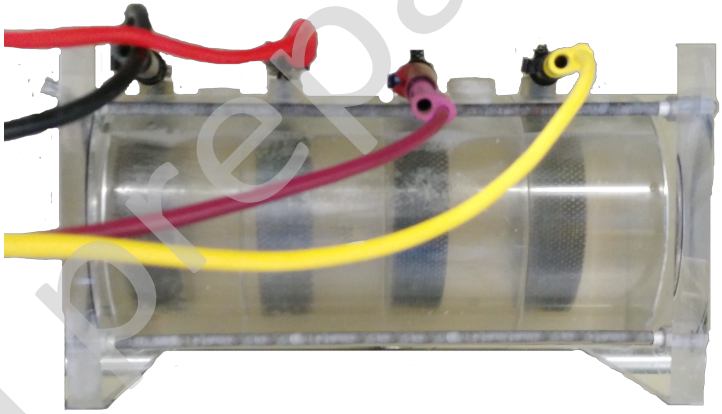
Graphical abstract



EK reactor for EOC removal from effluent in WWTP as a tertiary treatment:

- ✓ No pumps;
- ✓ No chemicals/reagents addition;
- ✓ Low energetic costs (0.6 €/m^3);
- ✓ High EOC removals (90%) with very different characteristics;
- ✓ Batch mode in a short period of time (2 hours).

Abstract

The presence of emerging organic contaminants (EOC) in the aquatic environment has been highlighted as a worldwide environmental problem due to their difficult elimination by conventional wastewater treatment processes. The present work investigates the feasibility of EOC removal from effluent by Electrokinetic technology (EK).

The nine target EOC under study were selected based on the most detected compounds in effluent and aquatic bodies in southern part of Europe (Portugal, Spain and France) and belong to the different classes: life style compounds, pharmaceuticals including hormones, personal care products and plasticizer.

The experiments with different anode materials (metal mixed oxide, MMO; and platinized coated titanium, Pt/Ti) and shape (bar, mesh and circular mesh) were carried out in a cylindrical reactor for 2 hours with 100 mA of current intensity. After selecting the best working anode, EOC removal efficiencies were studied as a function of the operating parameters: current intensity (125 and 175 mA) and also cathode influence. A proof of concept study showed the applicability of the electrochemical oxidation technique for larger scale use.

It was demonstrated that the effect of some operative parameters on the EK dramatically depends on both the nature of the electrode and of the EOC characteristics. Higher removals were obtained at MMO circular mesh anode with EOC removals range from 24% to <LOD. Caffeine and carbamazepine were the EOC most difficult to remove. The removals increased for these two EOC (up to 50%) when the cathode was replaced for the same material and shape as the best working anode previously found. The current intensity increase did not show to be advantageous for EOC removal in the here tested conditions.

Keywords: effluent; WWTP; emerging organic contaminants; electro-catalytic materials

Highlights:

- Comparative electro-oxidation efficiency of several anode materials was investigated;
- Influence of operating parameters, current density, and cathode was studied;
- EK set-up with MMO circular mesh as both anode and cathode showed removals up to 74 ± 14 % for all EOC;
- Proof-of-concept was carried and EOC removals close to 100% were achieved.

1. Introduction

The detection of emerging organic contaminants (EOC) in the environment has attracted the attention of researchers in the recent years (Ebele et al., 2017; Comber et al., 2018; Paíga et al., 2019). The EOC are products or chemicals without regulatory status and whose effects on environment and human health are still unknown or not completely understood.

The main source of EOC occurrence in the environment are the wastewater treatment plants (WWTP) that can eliminate or remove a substantial amount of these compounds, but there may still be significant concentrations of them in effluents discharged into surface water bodies (Verlicchi et al., 2012; Petrie et al., 2014; de Jesus Gaffney et al., 2017).

WWTP were primarily designed to serve the purpose of removing pathogens, suspended solids and gross organic and inorganic matter, rather than the removal of the increasing numbers of chemicals (e.g. pharmaceuticals and personal care products). Even though EOC are usually found in the aquatic environment at trace concentrations (i.e., between ng L-1 and µg L-1 or even lower, known as micropollutants), concerns are rising associated with antimicrobial resistance (Piña et al., 2018) and chronic impacts on biodiversity including endocrine disrupting effects on fish (Meador et al., 2016). Some other EOC effects are summarized in (Gogoi et al., 2018). The widespread occurrence of EOC in water has high probability of their incorporation in crops irrigated with contaminated effluent and possess risk to human health upon consumption due to the accumulation of EOC within crop plants (Ben Mordechay et al., 2018; Calderón-Preciado et al., 2011; Christou et al., 2017; Hurtado et al., 2017).

The treatment of urban wastewater is one of the biggest challenges of the twenty-first century. The recent investigations have examined EOC fate during wastewater treatment, focusing on their removal during conventional (e.g., activated sludge) and advanced (e.g., ozonation and membrane filtration) treatment processes. It is suggested that more exhaustive studies be led to fill knowledge gaps in the conduct of EOC under traditional sewage treatment and advanced treatment techniques (Gogoi et al., 2018). Research efforts are underway to develop more powerful oxidation methods than those currently applied in WWTP for achieving the complete destruction of EOC, but so far, successful mitigation strategies have not yet been established (Schröder et al., 2016).

The electrochemical methods for wastewater treatment offer a great advantage, since no additional chemicals are required as e.g. in electro-Fenton oxidation (Chu et al., 2012), and the electron may be considered as a "green," controllable reagent. The great effectiveness of the process is due to the production of hydroxyl radical (•OH), which is a non-selective, very powerful oxidizing agent (2.8 V) able to react with organics giving dehydrogenated or hydroxylated derivatives, up to their complete mineralization is reached (conversion into CO2, water and inorganic ions) (Tung et al., 2013). The electrochemical oxidation of organic pollutants can take place in two ways depending on the electrode surface: (i) direct electron exchange between the contaminant and the electrode surface, or (ii) by

indirect in situ electro generation of catalytic species, which are able to promote contaminant oxidation with their high oxidizing power (Wu et al., 2014). The effectiveness of anodic oxidation for wastewater treatment depends largely upon the properties of the anodes material and the organic substances involved in the process (Cui et al., 2009; Feng et al., 2014; Li et al., 2005). During the electrochemical oxidation process, several anodes favored the partial and selective oxidation of contaminants, while others favored complete conversion to CO2 (An et al., 2012).

The anode material has a strong influence on the selectivity and efficiency of the degradation process, their different behavior being explained by a model that assumes the existence of ‘‘active’’ and ‘‘non-active’’ anodes. Both kinds of anodes (M) oxidize the water forming the physisorbed hydroxyl radical (M(•OH)). This radical interacts strongly with the surface of the ‘‘active’’ anodes, being transformed into the chemisorbed “active oxygen” or superoxide MO, with the MO/M pair being a mediator in the electrochemical conversion of organic compounds; the surface of “non-active oxygen” anodes interact weakly with M(•OH) and this radical directly reacts with organics until total mineralization is achieved. Ruthenium dioxide, iridium dioxide, platinum, graphite are typical examples of “active anodes”, while lead dioxide, tin dioxide, BDD and sub-stoichiometric TiO2 electrodes can be considered as “non-active” electrodes, with the BDD anode being the most potent “non-active” anode known (Feier et al., 2018; Rivera-Utrilla et al., 2013). “Inactive” anodes are based on main group elements that do not form higher oxides and that have high overpotentials for evolution of O2 (g). Here, the sorbed hydroxyl radicals A∼OH• react directly with an oxidizable substrate, ultimately leading to mineralization, called electrochemical advanced oxidation process (EAOP) (Rueffer et al., 2011).

Electrochemical methods are considered by many to be a relatively new technology that is developing rapidly, thanks to the continuing discovery of new electrode materials and applications to ever more diverse industries. Among the different anode materials that have been tested, boron doped diamond (BDD) electrodes are well known for the high mineralization because of the highest production of •OH (Patel et al., 2013). Despite the BDD electrodes having the highest potential for •OH, lower efficiencies are observed for the BDD due to mass transport limitations for small concentrations of pollutants. In addition, the high price of BDD on a large scale is the major drawback, which is thwarting the widespread use because chemical vapor deposition is a basic requirement in the fabrication of the BDD electrodes which has restricted its application to small scale industries and limited large scale industrial applications (Brillas et al., 2005a; Patel et al., 2013).

Dimensionally stable anodes (DSA) that are prepared by the deposition of a thin layer of a mixture of active and inert metal oxides onto a base metal, usually titanium (Ti), are found to have varying degrees of success (Wu et al., 2014; Yuan et al., 2013; Zheng et al., 2011). The active oxides that consist of precious metal oxides (Ru, Ir, Pt) act as electro-catalyst, while the inert oxides modulate the electrochemical properties of the active components, providing high catalytic activity and higher life. DSA have been widely explored in the field of wastewater treatment due to their high surface area, high

catalytic activity, and high stability to anodic corrosion, excellent mechanical and chemical resistance and lower energy consumption (Comninellis and Pulgarin,1991.; Wu et al., 2014). The Pt/Ti anodes are widely used due to their very high quality and low-maintenance and was previously tested to remove EOC, as pharmaceuticals and personal care products (PPCPs) from effluent and sewage fresh sludge (Ferreira et al., 2018; Guedes et al., 2015).

The electrochemical removal of EOC from effluent by oxidation is the focus of the present work. The main goal is to improve effluent quality in WWTP as could work as a tertiary treatment, and contribute for (i) safe effluent discharge and (ii) effluent reuse decreasing water usage across the world to prevent water scarcity. For this purpose, five different anodes, in terms of material and shape were tested with a fixed cathode (titanium bar coated with MMO) in order to find the best EOC removals. The production rate of hydroxyl radicals on the above different catalytic electrodes was also done. The anode materials (MMO containing IrO2 and RuO2/Ti and Pt/Ti) were selected based on its expected electro-catalytic function for organic oxidation already known as very stable and due to the acid/alkaline and corrosion resistance. The proof of concept for the EK reactor with optimized conditions (anode, cathode and current intensity) was carried out. The target EOC were selected based on the most detected compounds (frequency and/or concentration) in effluent and/or aquatic bodies representative of the SUDOE area (Portugal and southern part of Spain and France): a) pharmaceuticals: sulfamethoxazole (antibiotic), diclofenac (anti-inflammatory), carbamazepine (anticonvulsive), estradiol and ethinylestradiol (synthetic estrogen), and b) personal care compound: oxybenzophenone (UV filter), "life style" compound: caffeine (central nervous system stimulant) and plasticizer: bisphenol A. The characteristics of the nine target contaminants can be seen in Table SM 1 of the supplementary material.

2. Materials and methods

2.1. Standards and chemicals

Solvents were from Merck (Darmstadt, Germany) and Sigma–Aldrich (Steinheim, Germany). Acetonitrile (ACN), methanol (MeOH), acetone, formic and acetic acid were HPLC grade. Deionized water was purified with a Milli-Q plus system from Millipore (Bedford, MA, USA). All standards were purchased from Sigma-Aldrich (Steinheim, Germany) with high purity grade (>97%).

Individual stock solutions for calibration purposes were prepared by dissolving each compound in MeOH at a concentration of 4000 mg L-1 and stored at 6 ºC.

2.2. Effluent sampling and characterization

Effluent samples were collected at a WWTP from Simarsul located in Quinta do Conde, Sesimbra, Portugal (38º34'13" N, 9º2'7" W). The WWTP has infrastructures with capacity to treat 19,300 m3

day-1 of urban wastewater, corresponding to about 94,000 equivalent inhabitants. The treated wastewater is discharged into Tagus river. The WWTP has an aerobic reactor of suspended biomass to allow the biological treatment of wastewater. The effluent from this reactor goes to the secondary settling tank for phase separation where liquid samples were collected.

The effluent samples were collected between April and July of 2018. The initial effluent characterization was performed by the WWTP and the main physicochemical characteristics of the effluent can be seen in Table SM 2 of the supplementary material.

All samples were transported in a cooling box from the WWTP to the laboratory and were kept at 6ºC in dark conditions. To remove colloidal particles, the effluent was pre-filtered using a 0.45-µm MF filter.

2.3. Electrochemical set-up

Electrochemical experiments for parameters test were carried out in a reactor cylindrical-shaped with a length of 10 cm (internal diameter of 8 cm; Figure 1). Electrodes were installed 2.5 cm from the middle of the reactor (5 cm apart from each other). The power supply (Hewlett Packard E3612A) was used to maintain a constant direct current. The effluent (450 mL) was spiked with a 2 mg L-1 of each EOC.

Initially, to select the best anode, experiments were made with a fixed cathode (activated titanium bar coated with MMO) and a total of five anodes (different shapes and materials, Table 1). The anode selection experiments (quadruplicates) were carried out for 2 hours, in dark conditions and controlled room temperature of 22°C with a current density of 0.3 mA cm-2.

The effluent used for each experiment, as well as, the variables of each assay are listed in Table 2.

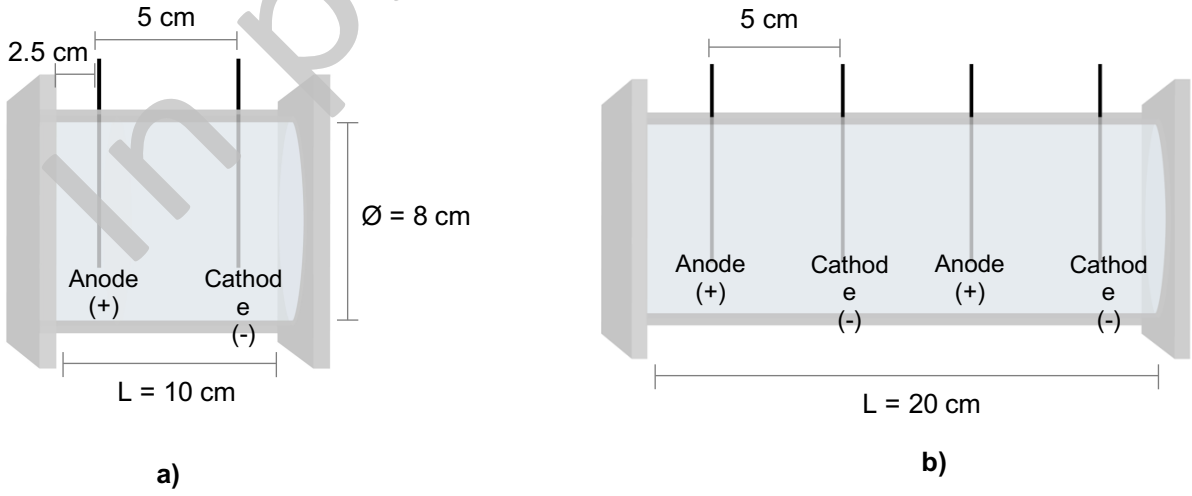


Figure 1 - Schematic representation of the laboratory reactor used in the experiments for effluent treatment a) testing the different parameters and the b) proof-of-concept set up.

Table 1 - Electrode material specifications

Material	Shape	Dimensions	Submerged area* (cm2)	Supplier
Pt/Ti	Bar	Ø = 3 mm L = 5.5 cm	5.32	Permascand®
MMO (IrO2+RuO2) coated titanium	Bar	Ø = 3 mm L = 5.5 cm	5.32	Force®
DSA Pt/Ti	Mesh	L = 6.0 cm W = 3.2 cm T = 0.2 cm	33.90	Inagasa®
DSA MMO (IrO2+RuO2) coated titanium	Mesh	L = 5.4 cm W = 2.9 cm T = 0.15 cm	22.50	Inagasa®
DSA MMO (IrO2+RuO2) coated titanium	Circular mesh	Ø = 6.0 cm W = 2 cm T = 0.1 cm	105.80	Force®

Legend:
L = Length; W = Width; Ø = Diameter; T = thickness
DSA: Dimensionally Stable Anode; MMO: Metal Mixed Oxide (Ir, Ru); Pt/Ti = Platinized titanium
* area that was in contact with the effluent while the experiment

After selecting the best anode, the current intensity (125 mA and 175 mA) was tested in order to find the best EK conditions for the final set-up.

The cathode was changed to match the anode in order to test the efficiency of the system. Effluent samples were taken every 30 minutes to study EOC removal kinetics.

Finally, with the best tested EK set-up, a scaling up of two fold was done for proof-of-concept. A electrochemical reactor of 20 cm long (internal diameter of 8 cm) and 900 mL of effluent were used. To account the doubled size, a sequence of four electrodes (anode-cathode; MMO circular mesh) were used interchangeably. The proof-of-concept (n=2) was carried out at 175 mA of current intensity (split in two) for 2 hours, in dark conditions and controlled room temperature (22 °C).

Experimental design took in consideration effluent sampling in different days to assure a robust EK system.

Conductivity, pH and the voltage drop between working electrodes were measured in the beginning and at the end of the experiments.

Table 2 - Experimental design and effluent samples used in each Electrokinetic (EK) experiment.

Goal	Experiment	Cathode		Anode		Effluent sample date	Effluent sampling #	Current intensity (mA)
		Material	Shape	Material	Shape			
Anode performance	EK 1.1	MMO	Bar	MMO	Bar	24.04.18	1	100
	EK 1.2	MMO	Bar	MMO	Bar	24.04.18	1	100
	EK 1.3	MMO	Bar	MMO	Bar	03.05.18	2	100
	EK 1.4	MMO	Bar	MMO	Bar	22.05.18	4	100
	EK 2.1	MMO	Bar	Pt/Ti	Bar	24.04.18	1	100
	EK 2.2	MMO	Bar	Pt/Ti	Bar	24.04.18	1	100
	EK 2.3	MMO	Bar	Pt/Ti	Bar	09.05.18	3	100
	EK 2.4	MMO	Bar	Pt/Ti	Bar	22.05.18	4	100
	EK 3.1	MMO	Bar	Pt/Ti	Mesh	24.04.18	1	100
	EK 3.2	MMO	Bar	Pt/Ti	Mesh	24.04.18	1	100
	EK 3.3	MMO	Bar	Pt/Ti	Mesh	03.05.18	2	100
	EK 4.1	MMO	Bar	MMO	Mesh	03.05.18	2	100
	EK 4.2	MMO	Bar	MMO	Mesh	03.05.18	2	100
	EK 4.3	MMO	Bar	MMO	Mesh	03.05.18	2	100
	EK 4.4	MMO	Bar	MMO	Mesh	22.05.18	4	100
	EK 5.1	MMO	Bar	MMO	Circular mesh	03.05.18	2	100
	EK 5.2	MMO	Bar	MMO	Circular mesh	09.05.18	3	100
	EK 5.3	MMO	Bar	MMO	Circular mesh	09.05.18	3	100
	EK 5.4	MMO	Bar	MMO	Circular mesh	22.05.18	4	100
Current influence	EK 5.5.1	MMO	Bar	MMO	Circular mesh	22.05.18	4	125
	EK 5.5.2	MMO	Bar	MMO	Circular mesh	22.05.18	4	125
	EK 5.5.3	MMO	Bar	MMO	Circular mesh	22.05.18	4	125
	EK 5.5.4	MMO	Bar	MMO	Circular mesh	17.07.18	6	125
	EK 5.6.1	MMO	Bar	MMO	Circular mesh	22.05.18	4	175
	EK 5.6.2	MMO	Bar	MMO	Circular mesh	12.07.18	6	175
	EK 5.6.3	MMO	Bar	MMO	Circular mesh	12.07.18	6	175
	EK 5.6.4	MMO	Bar	MMO	Circular mesh	17.07.18	7	175
Proof-of-concept	EK 6.1	MMO	Circular mesh	MMO	Circular mesh	05.06.18	5	100
	EK 6.2	MMO	Circular mesh	MMO	Circular mesh	05.06.18	5	100
Cathode influence	EK 7.1	MMO	Circular mesh	MMO	Circular mesh	12.07.18	6	100
	EK 7.2	MMO	Circular mesh	MMO	Circular mesh	12.07.18	6	100
	EK 7.3	MMO	Circular mesh	MMO	Circular mesh	17.07.18	7	100
	EK 7.4	MMO	Circular mesh	MMO	Circular mesh	17.07.18	7	100

2.5. EOC extraction and analysis

The effluent samples were pre-cleaned/concentrated by solid phase extraction (SPE) using Oasis HLB 500 mg (Waters; Saint-Quentin En Yvelines Cedex, France). The cartridges were placed in an SPE manifold connected to a vacuum pump and operated as follows: conditioned by washing with 3 x 6 mL of MeOH, followed by re-equilibrium with 3 x 6 mL of Milli-Q water; for EOCs enrichment, samples were acidified to pH 2 before extraction (nitric acid; deionized water, 1:1) , and filtered through 0.45 µm MF filter; 200 mL of sample was passed through the cartridge at a flow-rate of approx. 10 mL min-

1; then cartridges were dried for ca. 2 min by vacuum; finally extracts were eluted with 2 × 6 mL of MeOH. Whenever needed, extracts were concentrated under a gentle stream of nitrogen. Extracts were kept at 5 ºC until analysis. Before analysis, each sample was filtered through FILTER-LAB® polytetrafluoroethylene (PTFE) syringes filters (pore size of 0.45 µm), previously passed through MEOH.

EOC quantifications was performed in an Agilent 1260 Infinity II high-performance liquid chromatography (HPLC) equipped with a quaternary pump and auto-sampler (1260), and a diode array detector (DAD) and fluorescence detector (FLD) 1100 Series. The RP-18e column (Chromolith High Resolution, 100 mm x 4.6 mm; VWR, Darmstadt, Germany) was used for analytes separation. All HPLC runs were performed at a constant flow (1 mL min-1), in gradient mode, with the oven set to 36 ºC. A mixture of ACN/Mili-Q water/formic acid was used as eluents (A: 5/94.5/0.5 % and B: 94.5/5/0.5 %) with a gradient of 97% of A (0-15 min) followed by 95% of B, until 50 min, and 97% of A, until 55 min. For data process the LC OpenLab software was used. Calibration curve was performed in the range between 0.5 and 20 mg L-1. The correlation coefficient (R2) and the LD and LQ are supplementary material.

Whenever needed, extracts were analyzed by gas chromatography with time-of-flight mass spectrometers (GC–TOFMS; Pegasus BT, LECO).

The recoveries rates of the methods were between 80% and 102% for all EOCs except BPA and MBPh that was ca. 70%, upon estimation by HPLC analysis of reference extracts attained from effluent spiked with the standard EOCs mix (2 mg L-1) and T0h and T2h of contact time (data is in supplementary material).

2.6. Data analysis

Statistically significant differences among samples for 5% level of significance (95% confidence interval, $p<0.05$) were evaluated through one-Way ANOVA Tukey's multiple comparisons test, using GraphPad Prism software (version Prism 7).

3. Results and discussion

3.1. General results

The final pH, conductivity and voltage values of the experiments are in Table 3.21.

Initial effluent samples pH was 7.99 ± 0.15. After EK, pH slightly increased in the range of 0.12 as minimum and 0.9 maximum. The small changes in pH were expected because electric current was applied and the •OH generated by the catalytic electrode can form hydroxide ions, which might result in a pH increase (Tung et al., 2013). Also, the slightly changes in effluent pH could be due to the slow accumulation of carboxylic acids that are then oxidized by •OH in the mineralization process of EOC.

This fact is reported in (Wang et al., 2016) where pH of the solution decreased slowly from 5.2 to about 4.3 at ~30 min and increased to 5.7 at ~60 min during electrolysis.

The effect of pH, mainly the initial pH, on anodic oxidation has been well reported in literature as it can influence oxidation mechanisms and surface properties of photocatalysts, leading to adverse effects such as aggregation of semiconductor particles, repulsion force between organic compounds and photocatalyst surface or lower production of hydroxyl radicals e.g. (An et al., 2012; Pérez-Estrada et al., 2005). On other hand, (Brillas et al., 2005b) showed that paracetamol can be completely removed with Pt electrode and its kinetics follows a pseudo-first-order reaction with a constant rate independent of pH. The findings are diverse and sometimes even contradictory, depending on the types of target pollutants, types of anodes and also types of electrolytes (Pérez-Estrada et al., 2005; Tung et al., 2013). It should be pointed out that the here tested EK technology does not need any addition of reagents to change the pH and has the advantage of maintaining effluent pH, being an asset if, e.g., effluent is reused for agriculture irrigation.

The conductivity was kept somewhat constant throughout the experiments. As conductivity express an estimate of the number of free charges in a solution, and if the ions produced at the electrodes do not result in higher conductivity, a constant conductivity indicates that the concentration of other ions were decreased. In all cases, the voltage tends to slowly decrease indicating decreasing resistance over time, further supporting this hypothesis. It should be noted that MMO material allowed a significant reduction of cell potentials (voltage values lower than Pt/Ti).

Table 3 - pH, conductivity and voltage of the experiments and the respective initial values.

EK #	Anode material	Shape	pHi	pHf	Cond i (mS/cm)	Cond f (mS/cm)	Vi (V)	Vf (V)
1.1	MMO	bar	8.00	8.64	1.23	0.88	26.4	26.3
1.2	MMO	bar	8.00	8.56	1.23	1.09	26.4	26.2
1.3	MMO	bar	8.01	8.51	1.10	1.20	29.7	26.2
1.4	MMO	bar	8.29	8.47	1.45	1.40	23.2	21.0
2.1	Pt/Ti	bar	8.00	8.59	1.23	1.22	30.1	26.4
2.2	Pt/Ti	bar	8.00	8.6	1.23	1.22	30.4	26.5
2.3	Pt/Ti	bar	7.84	8.75	1.26	1.27	24.6	24.7
2.4	Pt/Ti	bar	8.29	8.53	1.45	1.38	24.5	24.1
3.1	Pt/Ti	Mesh	8.00	8.3	1.23	1.08	24.0	21.0
3.2	Pt/Ti	Mesh	8.00	8.12	1.23	1.15	23.9	21.4
3.3	Pt/Ti	Mesh	8.01	8.21	1.10	1.05	24.5	20.0
4.1	MMO	Mesh	7.91	8.28	1.10	1.02	20.2	19.6
4.2	MMO	Mesh	7.88	8.36	1.19	1.11	19.2	18.4
4.3	MMO	Mesh	8.01	8.42	1.15	1.29	22.9	19.0
4.4	MMO	Mesh	8.01	8.43	1.15	1.41	18.6	17.5
5.1	MMO	Circular	8.00	8.44	1.45	1.12	19.5	17.9

5.2	MMO	Circular	7.84	8.12	1.25	1.25	16.9	16.1
5.3	MMO	Circular	7.84	8.16	1.26	1.30	18.0	17.6
5.4	MMO	Circular	7.84	8.18	1.26	1.29	15.4	15.3

3.2. EOC removal

Differences among EOC removal were observed for the different electrode materials tested in the electrochemical reactor, ranked by increasing removal percentage:

- CAF and CBMP: 36±15% and 46±5% using Pt/Ti, but with MMO circular mesh similar ($p>0.05$) removals 44±6% to 49±10% were achieved;
- BPA, IBF and MBPh: between 59%±5% and 78±9%;
- SFM and DCF: approx. 90%;
- E2 and EE2: higher than 90% (below LD; 0.2 ppm).

The differences between the EOC removals can be mainly attributed to their structure, which influences the electrochemical degradation. It has been reported that •OH generated from water electrolysis, play a vital role in electrochemical oxidation mechanism of organic chemicals. A study with EE2 proved that •OH and radical chain reactions might be the main contribution for EE2 destruction in the electrochemical catalysis (Feng et al., 2010). In the present study, the analysis of effluent samples in GC–TOFMS revealed the presence of oxalic acid after EK treatment using MMO circular mesh as anode, which come from the destruction of the benzenic ring of aromatic pollutants by •OH (Brillas, 1998).

CAF and CBMP have a pKa higher than effluent pH (pKa of 14.0 and 13.9, respectively), which might influence degradation mechanisms. For electro-organics reactions one or two deprotonations must precede the electron transfer step with the electrode material. CAF and CBMP have a very stable protonated group, the tertiary amine of the ring and when the solution pH is smaller than molecule pKa, deprotonation is more difficult. It is thus possible to deduce that deprotonation might be the rate controlling reaction step, similarly to the antibiotic lincomycin (Carlesi Jara et al., 2007), where the slow overall abatement was explained by an intrinsically slow primary electron transfer and by the fact that chemical reaction coupling has to take place.

The other EOC were in their ionized form (pKa < pH), which make them more soluble and probably more available to •OH attack. (Pérez-Estrada et al., 2005) reported the importance of the pH lower than the pKa for DCF, in order to avoid the precipitation of the compound thus influencing the removal.

Table 0.1 - Presence (%) of EOC at the end of the EK treatment for the five anodes tested (n=4).

Anode material	EOC presence (%)								
	CAF	SFM	CBMP	BPA	E2	EE2	DCF	IBF	MBPh
MMO bar	96 ± 4	53 ± 20	92 ± 10	70 ± 19	56 ± 25	58 ± 26	60 ± 13	104 ± 5	74 ± 13
Pt/Ti bar	54 ± 5	25 ± 13	64 ± 15	55 ± 28	56 ± 22	46 ± 18	11 ± 3	41 ± 5	48 ± 25
Pt/Ti mesh	77 ± 1	62 ± 2	90 ± 3	65 ± 2	81 ± 5	87 ± 5	72 ± 2	89 ± 4	61 ± 2
MMO mesh	99 ± 14	60 ± 21	98 ± 8	71 ± 19	67 ± 15	72 ± 11	70 ± 15	114 ± 13	69 ± 21
MMO circular mesh	61 ± 10	9 ± 9	76 ± 6	30 ± 20	<LOD	<LOD	10 ± 2	48 ± 2	22 ± 9

Legend: bold values means the lowest presence for each EOC among the different EK experiment (MMO bar, Pt/Ti bar, Pt/Ti mesh; MMO mesh; MMO circular mesh)

It should be mentioned the variability of the effluent under study. As previously stated the experimental design took in consideration different sampling times and the differences on EOC removal between replicates of the same experiments might be correlated with the effluent characterization parameters. Positive correlations could be explained through the dissolved organic matter competition for the electrogenerated •OH, which is commonly characterized by BOD and COD values (Santos et al., 2009).

Due to the fluctuation of the effluent quality in WWTP it is of practical interest to examine how the initial effluent sample, e.g. COD value affects the EOC removal from effluent in EK-based technologies.

3.3. Electrodes performance

The five types of anodes performed considerably differently ($p<0.05$) in terms of EOC degradation (Table 3.22). The best result was obtained with MMO circular mesh followed by Pt/Ti anode bar, with MMO coupling good efficiencies with lower energy consumption (Table 3.26). The other three electrodes had a similar performance in terms of EOC removal with MMO bar having the lowest removals (from 0% to 53%± 20%).

It is well accepted that the use of an anode material with a high oxygen evolution potential is desirable for organic oxidation because of its inhibition of power losses to oxygen generation (Li et al., 2005).

The differences among the electrodes can also be seen through the cyclic voltammetry and the chronopotentiometry. The MMO bar was used as counter electrode and saturated calomel electrode (SCE) as the reference electrode in 10-3 M NaNO3 at scan rate of 100 mV s-1.

The oxygen evolution potentials of the four working anodes were determined using cyclic voltammetry (SCE: *saturated calomel electrode*

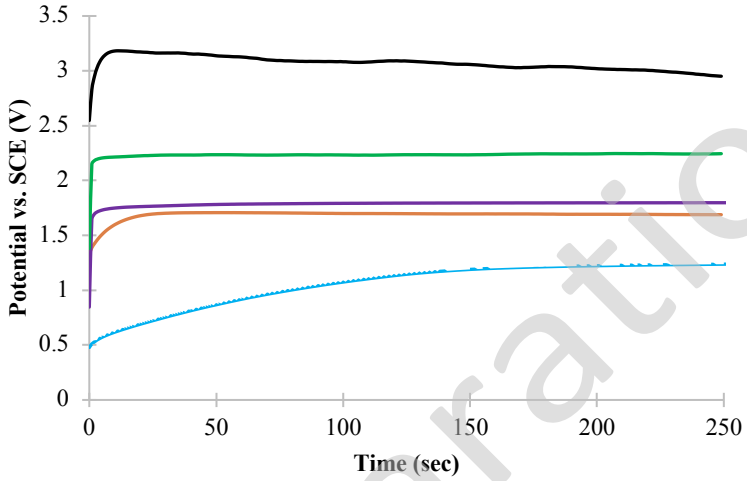
). The anodic oxidation potential was very different following the anode material. The domain for Pt/Ti mesh and bar was at 1.2 and 1.5 V vs. Ag/AgCl, respectively. But for MMO where a steady increase of the current is observed the definition of the electroactivity domain was difficult.

According to the chrono potentiometry results, the MMO circular mesh anode has by far the highest anode working potential and the MMO bar the lowest working potential taking more time to reach the potential at 0.5 mA cm-2. The low anode potential of MMO bar is probably related with the low •OH generation during the EK process, and thus it demonstrated the lowest effectiveness for EOC degradation. The use of a circular mesh provided a higher surface area to volume ratio (Table 2.7) and thus, compared to the other anodes tested, greater potential for •OH production, and subsequently faster and stronger EOC degradation. This is supported by the results attained for the MMO circular mesh compared to the bar that presented less between 53% ± 20 – 104% ± 5 EOCs removals Table 3.22.

The exact catalytic role of the anode surface in organic oxidation is still under discussion. It is generally believed that organic compounds in aqueous solutions can be oxidized on an anode by direct electron transfer and indirect oxygen atom transfer. In the direct electron transfer process, organics are adsorbed on the anode surface and give up electrons to the anode. With the indirect oxygen atom transfer, it is generally considered that oxygen radicals, especially the •OH generated from water electrolysis, play a critical role in the EOC oxidation mechanism of organic substances. The direct anodic oxidation is attractive because it does not need chemical additives, which may cause secondary pollution. The main problem during direct anodic oxidation is the deactivation of the anode surface, due to the formation of polymer on the surface (Li et al., 2005). In the present work, the surface of the electrodes appeared to affect the EOC oxidation mechanisms, when comparing the Pt/Ti bar and mesh (Table 3.22). In terms of EOC oxidation, the Pt/Ti bar showed better performance than the mesh and similar to the MMO circular mesh. In addition to •OH generation, the electrodes surface might have a property that is favourable to the adsorption and direct oxidation organics. These electrodes could be somewhat less efficient in the adsorption of small organic molecules and in electron transfer from the organic to the anodes. In the anodic oxidation process, active sites on the anode surface may participate in •OH production, whereas other sites function in the adsorption and activation of organic molecules. Therefore, the greater the number of active sites the higher is the catalytic ability of an anode (Cui et al., 2009). Organic species have the tendency to adsorb on the platinum electrode surface, as well as, by its easy generation of active oxygen species (Carlesi Jara et al., 2007). However, adsorption interactions between organic compounds and anode material and formation of a polymer layer on the anode surface can lead to the deactivation of the anode (poisoning effect) (Panizza and Cerisola, 2009). Thus, the oxidation signal disappears due to the possible formation of a polymeric film on the surface of the electrode. In organic wastewater treatment, anodic oxygen evolution actually causes a power loss, which reduces the overall current efficiency for both direct and indirect organic oxidation (Stucki et al., 1991). Therefore, the use of an anode material with a high oxygen evolution potential is especially desirable since it can decrease the unwanted power loss to oxygen generation. A better adsorption of the organic on the anode surface improves electron transfer for direct organic oxidation and allow a more effective indirect oxidation by the hydroxyl radicals generated on the anode. The experimental

results suggest that the different anode surfaces have different degrees of reactivity towards EOC degradation.

The generation of •OH from water electrolysis is largely responsible for the destruction of most organic chemicals during the EK process (Terashima et al., 2002). The difference in the effectiveness and performance of different anode materials for wastewater treatment demonstrates the complexity of the EOC reaction mechanisms involved. It is important to pointed that at the end of the experiments all the anode materials showed to be resistant to corrosion to the current applied.



SCE: saturated calomel electrode

Figure 2 - Electrochemical properties of the five different electrodes: chrono potentiometry for the anodic potentials and the current density of 0.5 mA cm-2.

3.4. Set-up optimization

3.4.1. Current effect

The results regarding the experiments with different current intensities can be seen in Figure 3.29. Current intensity is considered an important operating parameter in electrochemical oxidation of organics at MMO anodes, for the purpose of both mechanistic study and cost-effectiveness analysis (Wu et al., 2014). It is reported that mineralization increases with current intensity (Brillas et al., 2005a). However, in literature is not linear that higher current intensity will be more efficient for all the processes. In the present work, increasing the current intensity (125 vs. 175 mA) had a positive influence (without statistical differences; $p>0.05$) only for the compounds that already showed higher removals with 100 mA. On the other hand, CAF, CBMP and IBF had a similar removals between the two current intensities tested and comparing with 100 mA. The increase of the current promote the direct anodic oxidation of pollutants, but also enhance the production of hydroxyl radicals (Brillas et al., 2005a; Tung et al., 2013). Therefore, efficiency drops since too high current density can increase the portion of current wasted due to the increase of secondary reactions (such as oxygen evolution at

the anode and H2 evolution at the cathode) (Panizza and Cerisola, 2009). This result indicates that current intensity did not influence the efficiency of the EOC mineralization in the tested conditions, with MMO anode suggesting a significant role of mediated processes. In (Sopaj et al., 2015) the current density did not influence the efficiency of amoxicillin mineralization with DSA (Ti/RuO2–IrO2) anode electrode and the authors suggested a significant role of mediated processes.

In the present study the trends observed for MMO circular mesh electrode, clearly indicated that the process is more efficient working under lower current densities, showing typical behavior of a diffusion-controlled process in which, a higher current intensity leads to lower efficiencies due to the occurrence of wasting reactions. Hence from above suggestion, a current of 100 mA with a submerged electrode area of 105.80 cm2 was chosen for the proof-of-concept.

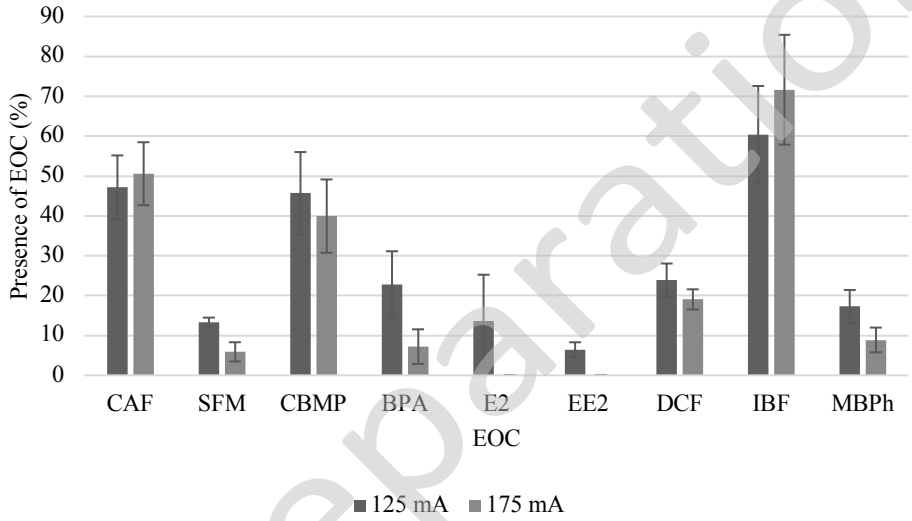


Figure 3 - Different current densities tested with the best anode material and shape for EOC removal previously tested (MMO circular mesh) (n=3).

3.4.2. Cathode influence

The voltage, pH and conductivity are shown in Table 5.

Table 5 - pH, conductivity and voltage drop for the EK treatment using MMO circular mesh as anode and cathode.

Replicate (n=4)	pHi	pHf	Condi (mS/cm)	Condf (mS/cm)	Voltage initial	Voltage final
EK 7.1	8.05	8.42	1.15	1.13	10.7	10.0
EK 7.2	8.05	8.42	1.15	1.01	11.4	10.8
EK 7.3	7.91	7.74	1.18	1.01	9.8	10.1

EK 7.4	7.91	7.74	1.18	1.04	9.3	9.6

The removals of EOC are presented in Figure 3.31. The MMO circular mesh both as anode and cathode showed removals between 74% ±15 and 94% ±8. Comparing with the MMO bar as cathode, significantly differences ($p<0.05$) were found for the EOC that showed to be more difficult to remove: CAF and CBMP (35% and 50% of difference comparing with MMO bar, respectively). It was expected that the degradation of the compounds would increase with a higher surface area-to-volume ratio as stronger reactions are provided between the electrodes and the compounds may suffer anodic oxidation and/or cathodic reduction. These results indirectly demonstrate that anodic oxidation power was not the only reason for the different degradation rate and that cathode material and shape can affect organics degradation by reduction reactions (Chu et al., 2012).

In previous works, the choice of cathode also showed to have a significant influence on the efficiency of the process, particularly for H2O2 accumulation and Fe2+ regeneration. In a divided electrolytic system (Yuan et al., 2013) reported a minimal degradation of BPA in anodic compartment with addition of Fe2+, ruling out the contribution of anodic oxidation and the production of H2O2 at the MMO anode. In comparison, the degradation was significant in the cathodic compartment in the presence of Fe2+ and O2. The minimal degradation in the cathodic compartment in the absence of Fe2+ and O2 proves that BPA cannot be reduced by the direct cathodic reduction. But instead, H2O2 was produced from the reduction of O2 on Ti/MMO cathode, thereby contributing to bBPA degradation in the presence of Fe2+.

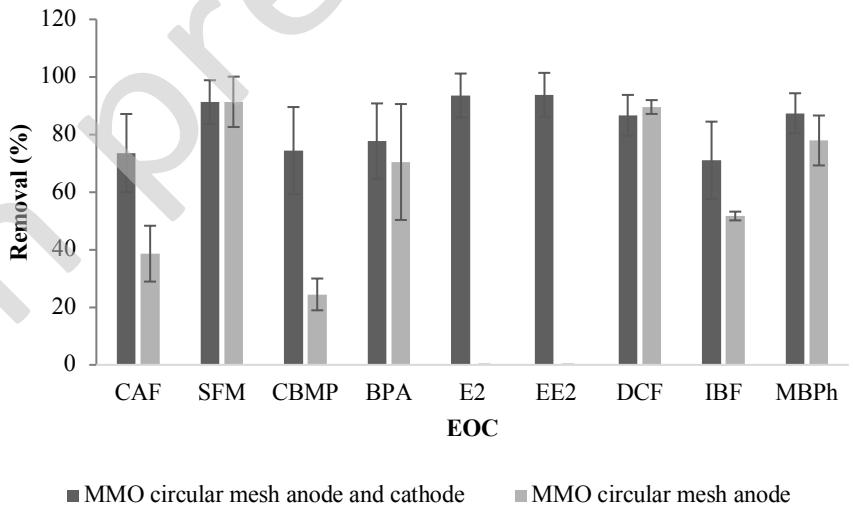


Figure 4 - EOC removals (%) by EK using MMO circular mesh as anode and cathode (n=4).

3.4.2.1. Proof-of-concept

The final set-up was decided having in mind the results previously obtained. The optimum operating conditions were set using the MMO circular mesh both as anode and cathode applying a current density of 0.3 mA cm-2 and running in batch of 2 hours each. Despite the doubled size, the same EOC removal efficiency was achieved, up to 90% for all the EOCs under study. The pH, conductivity and voltage drop are in Table 3.25.

Table 7 - pH, conductivity and voltage drop for the proof-of-concept (n=2).

pHi	pHf	Condi (mS/cm)	Condf (mS/cm)	ΔV (V)
7.82	7.75 1	1.40	1.33	0.1
7.82	8.24 1	1.40	1.26	0.2

[1] at 21.9 ºC

Once the EK treatment revealed positive results in the EOC removal, as described earlier, a prototype should be implemented in a WWTP as a tertiary effluent treatment. Besides the technical feasibility, the economic feasibility needs to be also considered for any technology to be suitable for use in the industry. To scale up the reactor in this study, the initial investment cost is not considered to be high as it needs a tank, electrodes and a power supply that can be connected to a solar panel. Comparing with the other electrode materials, one of the attractive advantages of the MMO electrodes, besides the high versatility, is the high energy efficiency and cost-effectiveness.

This can be verified when comparing to the energy consumption of Pt/Ti electrodes. The energetic consumption was calculated through the Equation 1 and the results are shown in Table 3.26.

Even using the MMO material, when replacing the bar to MMO circular mesh, the energy consumption spent went down 1.7 times than when using a bar (all data in Table X). This will positively reflect in the energy costs: 0.7 €/kWh instead of 1.1€/kWh. The MMO mesh circular has the energy consumption average of 0.7 €/m3 of effluent, which means 2. 5 times less than using Pt/Ti. Comparing with other treatments, also based on compounds oxidation, namely advanced oxidation process (Mahamuni and Adewuyi, 2010) the EK treatment proposed is much cheaper.

$$\boldsymbol{Energy\ consumption\ (kWh) = \frac{V \times A \times h}{1000}} \qquad \text{Equation 1}$$

V = cell voltage average, Volts

A = applied current, Amps

h = time of treatment, hours

Summing up the process under study has the main advantages of being: (i) simple to operate and to design; (ii) without addition of any reagent; (iii) handling low EOC concentrations; (iv) batch processes

in very short periods of time; (v) low investment cost; and (vi) possibility of water reuse (more studies are needed in order to guarantee all the regulated parameters).

Table 5 - Energetic costs for each effluent treatment by EK technology.

EK experiment	Voltage average (V)	Applied current (A)	Time (h)	Energy consumption (kWh)	Average (kWh)	€/m3 (*)	Average €/m3
1.1	26,35	0,1	2	0,00527	0,00513	1,8	1,7
1.2	26,30	0,1	2	0,00526		1,8	
1.3	27,95	0,1	2	0,00559		1,9	
1.4	22,10	0,1	2	0,00442		1,5	
2.1	28,25	0,1	2	0,00565	0,00528	1,9	1,8
2.2	28,45	0,1	2	0,00569		1,9	
2.3	24,65	0,1	2	0,00493		1,6	
2.4	24,30	0,1	2	0,00486		1,6	
3.1	22,50	0,1	2	0,0045	0,00449	1,5	1,5
3.2	22,65	0,1	2	0,00453		1,5	
3.3	22,25	0,1	2	0,00445		1,5	
4.1	19,90	0,1	2	0,00398	0,00388	1,3	1,3
4.2	18,80	0,1	2	0,00376		1,3	
4.3	20,95	0,1	2	0,00419		1,4	
4.4	18,05	0,1	2	0,00361		1,2	
5.1	18,70	0,1	2	0,00374	0,00342	1,2	1,1
5.2	16,50	0,1	2	0,00330		1,1	
5.3	17,80	0,1	2	0,00356		1,2	
5.4	15,35	0,1	2	0,00307		1,0	
6.1	10,35	0,1	2	0,00207	0,00207	0,7	0,7
6.2	11,10	0,1	2	0,00222		0,7	
6.3	9,95	0,1	2	0,00199		0,7	
6.4	9,95	0,1	2	0,00199		0,7	
7.2	7,15	0,175	2	0,00250	0,00248	0,4	0,6
7.3	7,00	0,175	2	0,00245		0,4	

(*) Considering an energy price of 0.15 €/kWh

4. Conclusions

The current work demonstrates that the electro-based technology scheme proposed here is a promising technology for being included in WWTP as a polishing step for EOC removal from effluent.

The choice of the anode material and shape showed to be an important parameter to improve the electrokinetic (EK) process not only for the EOC removal, but also to make a more efficient process in

terms of energy consumption. The replacement of cathode for the same material also showed to be relevant in the EK process increasing the removal of the EOC that showed to be more recalcitrant to degradation promoting an homogenous removal (74% ±15 and 94% ±8). The optimization of the current density applied to the electrolytic cell was also particularly important during the EK process, as the increase of the current density does not necessarily mean higher EOC and more efficient process.

The proof-of-concept was carried out with almost complete mineralization of all the EOC. The results achieved in this study show a different perspective regarding the MMO, Pt/Ti anode material, which have been reported to be less efficient than BDD. Based on the obtained results, the next step would be the scale up the process.

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Supplementary Material

Table SM 1 - Information of target EOC

EOC	Formula	MW (g/mol)	Log Kow a	pKa b	Sol. In water (mg/L)	UV abs (nm)	Category
Caffeine (CAF)	C8H10N4O2	194.19	-0.07	14.0 c	2.16×104 d	273	Central nervous system stimulant
Sulfamethoxazole (SFM)	C10H11N3O3S	253.279	0.89	5.7	610 f	268	Antibiotic
Carbamazepine (CBMP)	C15H12N2O	236.274	2.45	13.9	18 d	284	Anticonvulsive
Bisphenol A (BPA)	C15H16O2	228.29	3.32	9.6-11.3	120 d	277.1	Plasticizer
17β-oestradiol (E2)	C18H24O2	272.38	4.01	10.7	3.90 e	280	Estrogen
17α-ethinylestradiol (EE2)	C20H24O2	296.40	3.67	10.3	11.3 e	280	Estrogen
Diclofenac (DCF)	C14H11Cl2NO2	296.147	4.51	4.15	2.37 d	276	Anti-inflammatory
Oxybenzone (MBPh)	C14H12O3	228.25	3.82	7.56	69 d	288/329	UV filter
Ibuprofen (IBU)	C13H18O2	206.19	3.97	4.91	21 d	220	Anti-inflammatory

References:
http://pubchem.ncbi.nlm.nih.gov; www.SigmaAldrich.com
Notes:
[a] logarithm of the octanol- water partition coefficient; [b] logarithm of acid dissociation constant; [c] at 40 ◦C; [d] at 25 ◦C; [e] at 27 ◦C; [f] at 37 °C

Table SM 2 - Main physicochemical characteristics of the effluent collected after secondary treatment in WWTP

	EFFLUENT SAMPLES								
Parameter (units)	S 1	S 2	S 3	S 4	S 5	S 6	S 7	S 8	S 9
Date of sampling	24.04.18	03.05.18	09.05.18	22.05.18	05.06.17	12.07.18	17.07.18	19.07.18	27.07.18
Color	Pale yellow	Pale yellow	Pale yellow	Yellow	Yellow	Yellow	Yellow	Pale yellow	Pale yellow
Odor	Very weak	Very weak	Very weak	Strong	Strong	Strong	Very weak	Very weak	Very weak
pH	8.00	8.01	7.84	8.29	7.82	8.05	7.91	8.02	7.90
Conductivity (mS cm-1)	1.23	1.10	1.26	1.45	1.40	1.15	1.18	1.11	1.00
Total phosphorus – P (mg L-1)	NA	3.40*	0.80	7.2*	0.84	4.60*	2.50*	2.9*	1.1
Total chloride - Cl- (mg L-1)	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Total suspended solids - TSS (mg L-1)	30	47	20	68	20	92	< 10	< 10	< 10
Chemical oxygen demand - COD (mg O2 L-1)	71	139	75	175	75	258	30	30	31
5-day biochemical oxygen demand - BOD5 (mg O2 L-1)	18	50	18	70	18	45	< 3	< 3	8.8
NH4	NA	46.1*	41	NA	41	0.031	52.9*	NA	7
N total	NA	NA	39	NA	39	15	NA	NA	5.8

Notes:
NA: not analyzed

*Total phosphorus analysis was performed in HANNA Instruments Wastewater Multiparame